DECOMPOSITION OF ANION EXCHANGE RESINS
BY ALPHA AND GAMMA RADIATIONS

By

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Abstract.

The formation of anionic complexes of americium-241 and their absorptions on an anion exchange resin, namely Deacidite FF, a polystyrene based resin with quaternary ammonium functional group, have been studied. It was found that sufficient quantities of thiocyanate, chloride and nitrate complexes of americium could be absorbed onto the anion exchange resin to enable the study of alpha radiolyses of anion exchange resins.

Alpha-particle irradiations of nitrate and thiocyanate forms of resins have been carried out by absorption of americium on functional groups of resins. The degradation of anion exchange resins has also been studied by slurrying the resin with americium solutions. It was observed that under both the conditions, the extent of degradation at any dose was almost the same.

A dependence of the stability of the resin upon hydrogen ion concentration was noted for both alpha and gamma radiation, but was found to be more prominent in the latter case. Studies of the dependence of the radiation stability upon ionic forms of resins revealed that the stability is independent of the anionic forms, except for

γ-radiolysis of the nitrate form of resin. The comparative results of alpha and gamma radiolyses of anion exchange resins showed that alpha particles produced less damage than an equivalent dose of gamma photons.

A study of the effects of dose rate on the radiolyses of anion exchange resins has shown that the higher the dose rate, the smaller is the extent of decomposition for an equivalent total dose. This effect was found to be more prominent in alpha radiolyses of resins.

Finally, the direct and indirect effects of gamma radiation on anion exchange resins have been investigated by irradiating the resin under various conditions, e.g. variable water content, scavenger concentrations, etc., and it is established that 60% of the deamination during γ-radiolyses of resins occurs through a reaction involving hydrated electrons.

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CONTENTS.

CHAPTER 1.

INTRODUCTION.

A wide range of organic ion exchange resins is now available for industrial use and many of these have found extensive application in the field of nuclear technology. Such applications can be divided broadly into four groups.

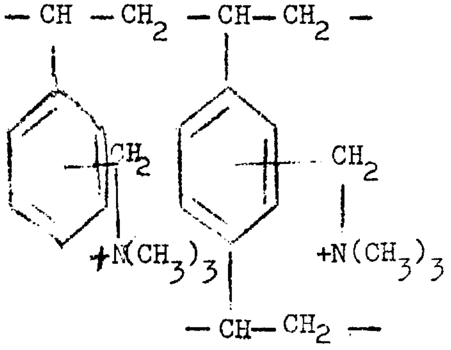
Processing of Raw Materials: separation and purification of uranium from raw materials (1, 2).

Chemical Processing of Irradiated Fuels: the separation of plutonium and fission products from irradiated fuels, subsequent purification of the plutonium(3, 4, 5), separation of americium and curium(6-8), the decontamination of radioactive waste solutions(9, 10).

Reactors: the control of pH and removal of corrosion products in the primary water coolant in a water cooled reactor; control of the pH and purity of heavy or light water moderators(11, 12).

Chemistry: many chemical separations of radioactive isotopes, often using chromatographic ion exchange e.g. separation of individual heavy elements(13, 14).

In the three latter applications, the ion exchange resin is exposed to ionising radiation and in some cases also to elevated temperatures. The radiation stability of anion exchange resins has been studied by several workers and reviews of this work have been made by Streat(15), Natarajan(16) and Creed(17). They have reported that aqueous slurries of the strong base anion exchange resin, Deacidite FF, undergo marked damage at γ-doses above 100 Mr. This resin can be represented as follows:



Irradiation causes loss of strong base capacity due to scission of the C—N bond and production of trimethyl amine. There is also a growth in weak base capacity due to conversion of some strong base groups to tertiary amine groups. Accompanying the changes in capacity, unusual effects have been observed with respect to the polymer matrix : changes in the cross-linking and, under some conditions, complete dissolution. Thus, Natarajan(16) has shown that the water regain (swelling weight) of the irradiated chloride and nitrate forms of resins decreases with increasing γ-dose when these are irradiated as slurries in water. The hydroxide form of resin, on the other hand, shows an increase in water regain up to a dose of 200 Mr., above which it decreases at a faster rate than in the former two resins. Irradiation of nitrate form of resin in 7M HNO_3 causes an unusual increase of water regain by the resin up to 500 Mr. and, above this dose, it decreases at a very fast rate. Irradiation under these conditions has shown that the resin is completely dissolved when subjected to a dose of 800 Mr. Creed(17) has studied the decomposition of the anion exchange resin by γ-irradiation at various temperatures, in the range of 25°C.-90°C., and has shown that the decomposition occurs to a greater extent than that due to the sum of the individual effects of temperature and radiation. Using a small column, he observed no significant increase in pressure in the resin bed up to 400 Mr.

More recently, further work on the irradiation of anion exchange resins has been reported(18-23). Irradiations have been carried out most frequently using cobalt gamma photons and, to a lesser extent, with x-rays, fast electrons and neutrons. It is of interest, however, to compare such studies with the results of irradiation by a radioactive isotope absorbed on the resin functional group. Natarajan(16) has reported some preliminary measurements using americium-241 absorbed on a cation exchanger (Zeocarb-225) in which he found that the alpha particles from the americium caused less severe damage to the resin than that resulting from an external gamma source. Recently, and after the work reported in this thesis was largely completed, Ahrens(24) reported the irradiation of the anion exchange resins Dowex 1, Permutit S1 and Permutit SK using plutonium-239 as the hexanitrato anionic plutonium complex absorbed on the resin in presence of 7M HNO_3. He also found the alpha particle damage to be less than that resulting from gamma irradiation, but was not able to explain satisfactorily this effect. Ahrens' analyses are based primarily on capacity measurements and do not include a detailed analysis of the degradation products.

The purpose of this work was to examine more completely the decomposition of anion exchange resins irradiated by an external gamma source and by an alpha-active isotope. In the latter case, the isotope was either absorbed on the resin or present dissolved in the slurrying liquid. The dependence of the extent of radiation damage on anionic form, acidity of the medium and dose rate effects have been investigated. Further experiments designed to improve understanding of the radiation chemical mechanisms for decomposition have been carried out.

CHAPTER 2.

ANION COMPLEXES OF AMERICIUM AND THEIR ABSORPTION ON ANION EXCHANGE RESINS.

2.1. Introduction.

Previous work(15-17) has shown that doses to the anion exchange resins of 50 to several hundred megarads are required in order to study the resulting decomposition. The application of beta-emitting isotopes was not considered suitable in view of handling problems and also expected difficulties in calculating the absorbed dose. Alpha-emitting isotopes present less problem with respect to dosimetry as all the alpha particles will be absorbed within the resin slurry, but appreciable problems in radiological protection arise. The only materials which could be considered here were plutonium-239 or americium-241. In the former, calculations based on the half life and alpha particle energy indicate that a dose of 30 Mr/month can be obtained if the anion exchanger is saturated with plutonium in the form of the hexanitrate ion (capacity assumed to be 4.0 meq/g). This relatively low dose leads to very long periods of irradiation which was unacceptable as only 100 mg. of plutonium were available. On the other hand, 200 mg. of americium-241 (half life 458 years, alpha particle energy 5.48 Mev) were available and so dose rates of about fifty times greater were feasible. With americium, however, little is known about its anionic complexes and, for this reason, Natarajan(16) confined his studies to the absorption of the trivalent americium cation. Preliminary studies of possible anionic complexes were therefore made.

Literature survey shows that americium dissolved in HCl, HNO_3 and H_2SO_4 could not be absorbed on an anion exchange resin(25, 26). Americium has been reported to form an anionic complex in 20M LiCl, which is absorbed onto the resin(27, 28). The resin however floats on the dense liquid. Americium is also absorbed by an anion exchange resin as a thiocyanate complex in 5-8M NH_4SCN solution(29-33), but the thiocyanate ion was reported to be decomposed by radiation(32-33) and hence americium might be lost from the resin due to the decomposition of its complex. Recently the absorption of americium as nitrate complex on the anion exchange resin was reported(13), although the Kd values are in disagreement with others.(34, 35).

It has been established that americium can be eluted from cation exchange resins by citrate(36) and even more easily by lactate, tartrate(37,38) and α-hydroxyisobutyrate(39,40), but no study has so far been made as to whether or not americium can be absorbed onto the anion exchange resins from these solutions. The existence of negative complexes in solution phases, such as acetic, glycolic and thioglycolic acids have been reported(40). Americium has also been reported to be existing as $Am(C_2O_4)_2^-$, $Am(HC_2O_4)_4^-$ and as an anionic complex with EDTA(41). The latter is not suitable since amine is the major product in the degradation of the resin to be studied. From the above information it is clear that an investigation was required to find a suitable system for alpha particle irradiation of an anion exchanged resin by absorption of an anionic complex onto it.

In this investigation, therefore, the formation of negative complexes of americium and its absorption onto an anion exchange resin has been studied by using lactate, acetate, oxalate, α-hydroxyisobutyrate, thiocyanate, chloride and nitrate complexes. Kd values of thiocyanate and nitrate complexes were also determined using milligram quantities of americium.

2.2. Experimental.

2.2.1. Preparation of americium solution.

The stock solution of americum in 7M HNO_3, available in this laboratory, was pure. It was precipitated as $Am(OH)_3$ by addition of NaOH, centrifuged and the supernatant solution was removed. The precipitate was washed 3 to 4 times with distilled water and finally dissolved in 0.1N HNO_3, made to a definite volume and estimated by alpha counting using a scintillation counter.

2.2.2. Preparation of H^+ form of Zeocarb-225.

About 5.0 g. of the Na^+ form of Zeocarb-225 was washed with water and warm methanol. An excess of 4% HNO_3 solution was passed through the resin bed in a column. The H^+ form of Zeocarb-225 thus obtained was water washed to remove HNO_3, dried overnight at 105°C. and stored in a stoppered bottle.

2.2.3. Preparation of different forms of anion exchange resins.

Deacidite FF 7-9% cross-linked, 100-200 mesh, was supplied in the chloride form. The resin was well washed with distilled water to remove water soluble impurities. It was then further washed with warm methanol. As some of the chloride ions,particularly those associated with weak base groups, might have been hydrolysed during washings, about 20 bed volumes of 4% HCl solution was then passed through the resin. The excess HCl was removed by a further methanol wash. The chloride resin thus obtained was then dried at 105°C. for 4-5 hours and stored for further use.

Other forms of the resin have been prepared from the purified chloride form of resin. For example, the nitrate form of the resin was prepared by passing 4% w/v $NaNO_3$ solution through a 5.0g. sample of the chloride form of resin in a column until the eluate was free of chloride ions. At this stage, the strong base groups were converted to nitrate. About 100 ml. of 4% HNO_3 solution was then passed until the eluate was completely free of chloride ions and the weak base groups were converted to the nitrate. Excess HNO_3 was removed by a methanol wash.

The conversions to oxalate, lactate, citrate and α-hydroxyisobutyrate were accomplished in a similar manner. Thus 4% w/v solutions of sodium oxalate, sodium lactate, sodium citrate and ammonium α-hydroxyisobutyrate solutions were used respectively to exchange the strong base chloride ions. The weak base groups were exchanged by using appropriate 4% acid. Conversion to thiocyanate form was accomplished by passing 4% NH_4SCN solution through the resin bed. The adherent ions were removed by a methanol wash. In this case the form of weak base group is not known.

2.2.4. Preparation of complexing solutions.

Sodium oxalate, sodium lactate and sodium acetate solutions of required molarities and pH (ref. table 2.1.) were prepared by dissolving the calculated amounts of respective acids and adjusting the pH by addition of sodium hydroxide solution. Ammonium α-hydroxyisobutyrate was prepared in the same manner, but by addition of NH_4OH solution instead of the NaOH. Other solutions used for complexing americium-241 were 5M NH_4SCN, 20M LiCl and 8M $LiNO_3$.

2.2.5. Preparation of complex solutions of americium and their absorption on resins.

Americium in mg. quantities dissolved in 0.1N HNO_3 was absorbed in about 0.05g. H^+ form of Zeocarb-225. The resin loaded with americium as cation was washed free of HNO_3. 2 mls. of a complexing solution, e.g. ammonium α-hydroxyisobutyrate was equilibrated with the cation exchange resin when most of the americium distributed itself to the solution phase. The α-hydroxyisobutyrate complex of americium was then separated from the cation exchanger and equilibrated with 0.1g. of α-hydroxyisobutyrate form of resin. The absorption of americium onto the anion resin was obtained from the measured amounts of americium in the resin and aqueous phases.

Similar methods for absorption of americium onto anion resins were employed using other complexing solutions, e.g. sodium lactate, sodium acetate, sodium oxalate, ammonium thiocyanate, lithium chloride and lithium nitrate. In case of oxalate, precipitation of americium was observed, when it was eluted from the cation exchange resin. It was observed that americium was considerably absorbed onto the anion exchange resin when LiCl, $LiNO_3$ and NH_4SCN solutions were used (Table 2.1.).

A more quantitative study to determine Kd was made using these solutions.

2.2.6. Determination Kd using LiCl, $LiNO_3$ and NH_4SCN solutions.

Method 1: This method is similar to 2.2.5. except that 5×10^{-3} ml. solution containing 10-20 μg. americium (instead of mg. quantities) was used for absorption onto the Zeocarb-225. After absorption of an anion complex of americium on the anion exchange resin, estimations of americium in the resin and solution phases were used to calculate the Kd values from the relation:

$$Kd = \frac{\text{Am/g. resin}}{\text{Am/g. solution}} .$$

Method 2: 5×10^{-3} ml. solution containing 10-20 μg. americium in 0.1N HNO_3 was added to 1 ml. of a complexing solution, e.g. 5M NH_4SCN, 20M LiCl and 8M $LiNO_3$. This was then equilibrated overnight with 0.1g. of the anion exchange resin in the appropriate form. Kd values were then calculated from the distribution of americium into the two phases. The Kd values determined by the two methods were found to be of the same order.

Table 2.1. Absorption of americium complexes on anion resins at varying pH and molarities of complexing solutions.

Complexing solution.	Molarity of complexing solution.	pH	Form of resin.	Am. absorption in resin phase.
Sodium oxalate	1.0	4.0	Lactate	Nil
	3.5	2.5	Lactate	Nil
	5.0	4.0	Lactate	Nil
	3.5	4.0	Thiocyanate	Nil
	3.5	4.0	Citrate	Nil
	3.5	4.0	Chloride	Nil
	1.8	10.0	Lactate	gradual precipitation of americium occurs.
	1.8	10.0	Chloride	-do-
			Thiocyanate	-do-
Sodium acetate	0.1	3.5	Oxalate	precipitation of americium occurs.
	0.05	(10M HNO$_3$).	Oxalate	No absorption.
Sodium Acetate	5.0	3.0	Citrate	0.53 mg/ 0.1g. resin.

(Table 2.1 - contd.).

Complexing solution.	Molarity of complexing solution.	pH	Form of resin.	Am absorption in resin phase.
Ammonium α-hydroxyisobutyrate.	0.5	4.0	α-hydroxyisobutyrate	Nil
	5.0	2.0	"	Nil
	5.0	4.0	"	Nil
	1.6	4.0	Citrate	0.45 mg/ 0.1g.resin.
NH_4SCN	5M	2-3	Thiocyanate	high absorption of americium. See Table 2.2.
LiCl	20M	5-6	Chloride	
$LiNO_3$	8M	3-4	Nitrate	

Table 2.2. Distribution coefficient, Kd, of americium in anion exchange resin.

Complexing solution.	Molarity of complexing solution.	pH/or acid molarity.	Am.absorbed per g. resin. µg	Am.in solution. µg /g	Kd	Mean Kd
NH_4SCN	5	1-2	523	3.4	154	190
	5	1-2	240	1.05	229.0	
	5	1-2	257	1.70	151	
	5	1-2	370	1.68	220	
	5	5-6	71x10^3	3.34 x 10^2	210	
	5	5-6	43.6x10^3	1.73 x 10^2	245	220
	5	5-6	60.4x10^3	3.1 x 10^2	195	
	5	5-6	57.8x10^3	2.5 x 10^2	230	
LiCl	19	5-6	350	3.6	97	
	20	5-6	277	2.1	132	

(Table 2.2 - contd.).

Complexing solution.	Molarity of complexing solution.	pH/or acid molarity.	Am. absorbed per g. resin. μg	Am. in solution. μg/g	Kd	Mean Kd
$LiNO_3$	8.0	1×10^{-3}M	248.0	2.84	87.0	90.5
	8.0	1×10^{-3}M	191.5	2.20	94.0	
	7.5	5×10^{-3}M	183.0	3.50	52.2	50.1
	7.5	5×10^{-3}M	182.0	3.78	48.0	
	7.5	5×10^{-2}M	160.0	3.3	48.5	53.7
	7.5	5×10^{-2}M	185.0	3.12	59.0	
	7.5	5×10^{-1}M	202.0	5.3	38.0	37.75
	7.5	5×10^{-1}M	186.0	4.96	37.5	
	7.5	5×10^{-3}M	67.7×10^{3}	1.6×10^{3}	42.5	44.2
	7.5	5×10^{-3}M	71.6×10^{3}	1.79×10^{3}	45.0	
	7.5	5×10^{-3}M	70.0×10^{3}	1.78×10^{3}	45.4	

2.3. Results and Discussion.

The high degree of separation of the trivalent actinide ions from one another, obtainable by elution from cation exchange resins using citric, lactic, tartaric and α-hydroxyisobutyric acids, is well known(14). These separations depend more on the differences in complexing powers of the eluants towards the metal than any specificity in the resins. Possible reactions in solution are :

$$M^{3+} + X^{-} \rightleftharpoons MX^{2+} \qquad (i)$$
$$MX^{2+} + X^{-} \rightleftharpoons MX_2^{+} \qquad (ii)$$
$$MX_2^{+} + X^{-} \rightleftharpoons MX_3 \qquad (iii)$$
$$MX_3 + X^{-} \rightleftharpoons MX_4^{-} \qquad (iv)$$

where M and X represent an actinide metal ion and a complexing anion respectively. It is likely that in the eluates sufficient MX_4^- may be present to be absorbed on an anion exchange resin. When such species are equilibrated with an anion exchange resin, the slight absorption of MX_4^- may shift the equilibrium in the aqueous phase resulting in the formation of more and more MX_4^- until finally an equilibrium is reached for MX_4^- between the aqueous and resin phases. Slight absorption of the α-hydroxyisobutyrate complexes of Cm^{+3} and Cf^{+3} onto an anion exchange resin was noted by Holm (42).

In the present work, it has been shown that lactate solutions of 1-5M concentration and at pH 2.5-10 and also the α-hydroxyisobutyrate at 0.5 and 5.0M concentration at pH 4, both fail to produce any measurable anionic products (Table 2.1). There is some absorption (about 0.5 mg/0.1g. resin) when the resin in the citrate form is equilibrated with acetate or α-hydroxyisobutyrate complexes of americium at pH 3 and 4, respectively. The absorption is so low, however, that only a dose to the resin slurry of approximately 1-2 Mr/day can be achieved.

When americium is eluted from a cation exchange resin by sodium oxalate solution, a clear solution of 3-5 mg/ml. is obtained. Though at this stage, some of the americium might be present as $Am(C_2O_4)_2^-$ or $Am(HC_2O_4)_4^-$ ions as reported by Moskovin (41) and Levedev (31), the americium is gradually precipitated as $Am_2(C_2O_4)_3$. The precipitation favours the back reaction (iv), which will proceed until all the americium is precipitated out. When this precipitate was dissolved in 10M HNO_3 and the resulting solution equilibrated with anion exchange resin, no absorption of americium onto the resin was observed. It can be concluded that americium is not taken up by the anion exchange resin in the presence of lactate, α-hydroxyisobutyrate or oxalate complexing ions. This may be because either no anionic species are formed, or if formed, they are not taken up by the resin due to steric hindrance, or are unable to displace the anion already on the resin anionic groups.

High absorptions are noted with americium complexed by thiocyanate, chloride and nitrate ions. Surls and Choppin(30) found Kd values for americium in 0.5, 2.0 and 4.0M NH_4SCN solutions in the order of 20, 45 and 80 respectively. The extrapolated values at 5M and 10M NH_4SCN would be 115 and 315 respectively. In the present work, at 5M NH_4SCN concentration, when μg quantities of americium are used, the Kd values for americium are found to be in the range of 150-230, the average being 190. The differences may be attributed to the differences in acidity **or** may be due to slight variation in the concentration of NH_4SCN solution. The Kd values determined by absorption of mg. quantities of americium were found to be of the order of 200.

For the LiCl - Deacidite FF system at 19 and 20M LiCl, Kd values of 92 and 132 respectively were found. Hulet(27) obtained a Kd of 25 at 12M LiCl. The higher values observed here are almost certainly due to the higher concentration of LiCl.

The data published in the literature for Kd values for $LiNO_3$-anion exchange resin systems are contradictory. Marcus13) finds at 8M $LiNO_3$ a Kd value of 90, but much lower values (~ 20) have been observed by others(34, 35). In this work it has been found that decreases in H^+ concentrations increase the Kd values. The change in Kd in the H^+ concentration range 0.5 - 0.005 is not large (~ 40-55), but values up to 90 can be obtained if H^+ concentration is reduced to about 0.001M. (Table 2.2.).

From the foregoing it can be calculated that absorption of americium in the range of 50-100 mg/g. resin can readily be affected and, on the basis of the Kd values reported above, dose rates of 15-30 Mr/day can be attained. The nitrate and thiocyanate systems were selected for all irradiations where the dose arises from americium absorbed on the anion exchange groups.

CHAPTER 3.

DECOMPOSITION OF ANION EXCHANGE RESINS BY ALPHA AND GAMMA RADIATIONS.

3.1. Introduction.

Previous work on the effects of radiation on ion exchange resins(16,24) has indicated that for both cation and anion exchange resins, alpha particles produce less damage than an equivalent dose of gamma photons. This may be due to one or more of the following : inherent differences in the action of the different radiations on water and resin, the proximity of the alpha emitters to the resin functional group, the presence of a very heavy ion on the functional group or to the irradiation media. Some workers(43,44) have claimed a stability dependence on the anionic forms of the resin while others(45) have found no such effect. The effects of dose rate has not been investigated thoroughly and the scanty data published in the literature is conflicting(46,47). Some workers (44,48,49,50) expressed the views that degradation of anion exchange resin may occur through the radicals produced in the radiolysis of water.

This chapter is therefore devoted to irradiation of the anion exchange resins under a variety of conditions designed to attempt an understanding of the irradiation processes involved.

The following are examined:

1. Effects of absorbed americium on the stability of the anion exchange resins.
2. Radiation stability of different anionic forms.
3. Effects of hydrogen ion concentration on the stability of anion exchange resins.
4. Effect of dose rate in radiation induced decomposition of anion exchange resins.
5. Irradiation of dried resins.

3.2. Experimental.

3.2.1. α-particle irradiations of 'Deacidite FF'.

3.2.1.1. Absorption of americium thiocyanate complex on the anion exchange resin and its irradiation:

10-15 mg. of americium in approximately 0.1N HNO_3 solution was equilibrated with about 0.1g. of Zeocarb-225 cation exchanger in a centrifuge tube, for 10-15 minutes with occasional stirring by a platinum wire. The supernatant solution was removed and the resin was washed several times with distilled water. Americium in the supernatant and washings was estimated. The absorbed americium was then eluted from the resin by 3 batch-wise equilibrations, each with 1.0 ml. of 5M NH_4SCN solution. The small quantity of americium left in the resin was eluted separately by 5 ml. of 5M NH_4SCN and was estimated.

The first 3 ml. of the eluate, containing most of the americium as the thiocyanate complex, was then added to a known quantity of anion exchange resin (usually 0.1g.) in another centrifuge tube and equilibrated for 1 hour with occasional stirring. The absorption of americium onto the resin was observed by noting the difference in the counts of the two phases as shown by a γ-counter. The supernatant was removed after centrifuging, made to a definite volume and the americium was estimated. Thus the americium absorbed in the anion exchange resin was known. The centrifuge tube containing the resin with absorbed americium was stoppered and left long enough for the resin system to attain the required radiation dose.

Americium absorbed in the resin was separated at the completion of irradiation by a water wash and subsequent elution with 0.1N HCl solution. The eluate and washings were made up to a known volume and the americium content estimated.

Dried SCN^- form of resin was also irradiated by α-particles. Americium was absorbed in the resin by the method described above. Excess NH_4SCN solution was removed by a methanol wash. The centrifuge tube containing the resin with absorbed americium was then placed under an infra-red lamp, for slow evaporation of the alcohol. After the removal of most of the alcohol, the resin was dried under the lamp at 80° - 90°C. for 1 hour. The centrifuge was then stoppered and left long enough for the resin to attain the required radiation dose.

3.2.1.2. Absorption of the nitrate complex of americium on the anion exchange resin, estimation of americium and irradiation of the resin.

10 mg. of americium was precipitated as the hydroxide and washed several times with distilled water. It was then dissolved in the minimum quantity of 5N HNO_3 added by a micropipette. The solution was centrifuged and the clear solution added to $LiNO_3$ solution so as to make the total volume up to 1 ml. and the concentration of $LiNO_3$ to 8M.

The solution was equilibrated with about 0.10 g. of a known weight of the nitrate form of resin (prepared by the method described in 2.3. and dried at 80°C.), in a column for 1 hour, with occasional stirring by a platinum wire. The $LiNO_3$ solutions containing unabsorbed americium was pumped out, made to a definite volume and the americium was estimated. The amount of americium absorbed in the resin was known from the difference. In order to calculate the α-particle dose rate in the system, it was necessary to know the weight of the $LiNO_3$ solution left on the resin and this was determined by the following experiment.

A small glass column (7.5 cm. x 1.0 cm.) fitted with sintered glass filter, a B10 stopper at the top and a small stopcock at the bottom was dried and weighed. 0.1 g. of resin was transferred to it and 1 ml. of 8M $LiNO_3$ solution containing no americium was added and allowed to stand for 1 hour. The $LiNO_3$ solution was then pumped out. The wet resin and the column were weighed. From the known weight of the wet column, the weight of the wet resin was known and thus the uptake of $LiNO_3$ solution per g. of resin was determined. These columns were subsequently used for americium absorption in the resin and as the irradiation vessels.

After americium absorption in the resin, the stopcock at the bottom was closed and the top of the column was stoppered. It was then left in a lead beaker for the required time.

The dose rate per day was calculated from the amount of americium absorbed and weight of wet resin (Appendix 2.).

At the end of the irradiation period, the americium was eluted from the resin by 0.1N HCl. The eluate was made up to 10 ml. and americium was re-estimated.

3.2.1.3. α-particle irradiations of resins by using americium solution.

Nitrate, chloride and sulphate forms of resins have been irradiated by α-particles using americium solution in different known acid concentrations and dose rates.

A solution of 35-40 mg. americium per ml. was prepared by dissolving ~~the~~ $Am(OH)_3$ precipitate in a minimum quantity of approximately 5M HNO_3. The pH of the americium solution as tested by pH paper using trace amounts of the solution was found to be about 3.0. When a higher concentration of acid was required, the calculated amount of the acid was added to the known quantity of the americium.

The weight of the resin, the volume and concentration of the americium solution were so adjusted that the resin was just soaked with the solution and the system received the required alpha dose rate. A typical example of the resin irradiation is given below. About 0.1g. chloride form of resin was weighed in a dry centrifuge tube. Americium solution of required concentration and acidity was prepared in another centrifuge tube. After centrifuging the solution, 0.2 ml. of clear americium solution containing 7-8 mg. americium was added to the resin by using a micropipette. The resin soaked up the americium solution and was left in the stoppered centrifuge tube until the required dose was reached.

At the end of irradiation, the americium and the basic radiolytic products were separated from the resin by washing with 0.1N HCl and americium was estimated by alpha counting. Americium was then precipitated as $Am(OH)_3$ by addition of conc. NaOH and separated by centrifuging. The radiolytic products in NaOH solution were steam distilled in a fume hood to make the distillate free of contamination. It was found that the minute amine yield (0.01 -0.15 meq.) cannot be quantitatively steam distilled and product loss may be up to 50% of the total. A calibration curve for the amines recovered by steam distillation against the known quantities in the range of 0.01 to0.15 meq., has been used for calculating the radiolytic product yield. (Appendix 4.).

3.2.2. Cobalt-60 γ-irradiations of Deacidite FF.

3.2.2.1. Dosimetry.

The 800 curie cobalt-60 source was used for gamma irradiation of anion exchange resins. The dose rate at the irradiation position was determined using the Fricke dosimeter. Since a bulb type irradiation vessel was used for irradiating the resins, dosimetry has been carried out in the actual irradiation vessel using ferrous sulphate solution of the same volume as the swelled resin or the dried resin, as the case demanded.

Under the experimental condition (i.e. 13.5 cm. from the source platform and in contact with the source guide) a dose rate of 19.0 Mr/day was obtained. The dose rate in the system is approximately the same as in H_2O,as shown in the appendix 3. . Care was taken in all experiments to reproduce exactly the conditions of dose rate calibration.

3.2.2.2. Irradiations.

During irradiations of resin slurries, gas bubbles were formed and these were trapped within the resin bed. In a tube of uniform 1 cm. diameter the resin bed was pushed up the tube by the released gases and this caused uncertainty in dosimetry. This difficulty was overcome by using a bulb type irradiation vessel which consisted of a flat bottomed tube of one cm. i.d., provided with a bulb of 1.5 cm. i.d. at about 1 cm. from the bottom.

About 1.0 g. of dry resin was weighed into the irradiation vessel, 3 ml. of distilled water or the solution as required, was added and the resin slurry was irradiated at the fixed position to receive a dose of 19.0 Mr/day. The gases were observed as bubbles trapped between the resin particles after doses of 20 - 30 Mr. The gases have been tapped out at intervals of 2 days.

When the resin was irradiated in absence of water, the weight of the dry resin taken was approximately 2.0 g., in order that its volume corresponded to that of 1g. of resin slurried in aqueous solutions.

γ-irradiations have been carried out under the following conditions:

Medium of irradiation	Forms of Resin
5M NH_4SCN	SCN^- and $La(SCN)_4^-$
Water	Cl^-, $SO_4^{=}$ and $PO_4^{\equiv}$
Acid solution	Cl^- and $SO_4^{=}$
Dried resin	Cl^-, SCN^-

3.2.3. Conversion of Unirradiated resins to different forms.

Thiocyanate, nitrate and sulphate forms of resin have been prepared from the chloride form of resin by the method described in 2.2.3. The phosphate form was prepared by passing 4% H_3PO_4 solution through a bed of chloride form of resin in a column until all the chloride ions were eluted. The excess H_3PO_4 was removed by a methanol wash. The phosphate form of the resin was dried overnight in an oven at 80°C. The complete conversion of the chloride form of resin to the thiocyanate form was confirmed by testing the eluate by the bismuth oxychloride test(51) and the conversion to other forms by a $AgNO_3$ test.

The thiocyanate form resin was converted to $La(SCN)_4^-$ form by the following method.

About 40 g. of $La(NO)_3$, 3 H_2O was dissolved in 100 ml. of 5M NH_4SCN solution to produce the lanthanum thiocyanate complex.

$$La(NO_3)_3 + 4\ NH_4SCN \rightarrow NH_4^+ \left[La(SCN)_4^-\right]^- + 3\ NH_4NO_3.$$

The pinkish coloured solution was passed through a bed of 10 g. of SCN^- resin in a column when $La(SCN)_4^-$ ions gradually replaced SCN^- ions on the resin. The equilibrium constant for the reaction appeared to be rather small and the saturation of the resin with the complex ion can be achieved only by use of a large excess volume of the complex solution. The converted resin was then washed with methanol until no lanthanum was observed in the washing (oxalate test). The resin was dried at 105°C. for 4-5 hours. A sample of the resulting resin was treated with sodium sulphate solution to displace the anions and the eluate was tested for presence of nitrate ions. None were detected showing that due to the large excess of SCN^- and $La(SCN)^-$ ions, there was no partial conversion to nitrate form as might have been expected.

3.2.4. Analysis of the $La(SCN)_4^-$ form of resin.

A sample of the dried resin was weighed, transferred to a column and was eluted with dil. HCl until all the

the lanthanum has been removed from the resin. The eluate was made up to a known volume and the lanthanum was estimated by the oxalate method (52). Finally, the resin was reconverted to the SCN^- form by passing 4% NH_4SCN solution. The resin was washed free of adherent NH_4SCN solution, dried and weighed. The capacity of the resin was then calculated on the basis of the dry weight of the thiocyanate form of the resin.

3.2.5. Capacity determination of unirradiated and irradiated resins.

Strong base and weak base capacities of all the forms of resins have been determined by the modified Fisher-Kunin method(53,54).

The strong base groups of both the irradiated and unirradiated resins have been converted to chloride form by using 4% NaCl solution and the weak base groups have been converted to the hydrochloride form by subsequently passing 4% HCl solution.

The HCl solution was removed from the resin by repeated washings with methanol. The complete conversion of the sulphate and phosphate forms of the resin have been confirmed by barium chloride and ammonium phosphomolybdate tests **respectively**. 80 ml. of 0.70% v/v of NH_4OH solution was passed through a bed of 1-2 g. resin (dry weight) at a rate of approximately 2 ml./minute . The resin was then washed free of NH_4OH solution with water. The elutate and the washings were made up to 100 ml. and the chloride concentration estimated by Volhard's method. This chloride arises from the weak base chloride together with chloride from part of the strong base groups hydrolysed by NH_4OH and water.

100 ml. of 4% w/v Na_2SO_4 solution was then passed through the resin bed when all the remaining chloride ions were eluted from the resin ($AgNO_3$ test). The eluate contained the strong base chloride ions and any strong base ions which were formed by hydrolysis. 10 ml. aliquots of this solution were used for chloride estimation and 50 ml. aliquots were titrated against N/10 HCl using methyl red indicators to estimate the hydroxyl ion concentration.

The capacity was calculated as follows:

Measured weak base = Weak Base + part strong base hydrolysed.

= X meq/g.

OH^- in Na_2SO_4 eluate = Y meq/g.

$\therefore$ Weak base corrected = (X-Y) meq/g.

Measured strong base in Na_2SO_4 eluate. = Z meq/g.

$\therefore$ Corrected strong base = (Z+Y) meq/g.

It may be noted that in the irradiations by α-particles, 0.1 g. of resin was used. During the capacity determination, 25 ml. volumes of NH_4OH and Na_2SO_4 solutions were used at a flow rate of 1 ml./minute.

3.2.6. Estimation of amines and ammonia.

Tertiary amine in presence of secondary amine was estimated by Dyer's method (55) as developed by Streat and Natarajan(15,16). The cupric dimethyl dithiocarbamate method(56) was employed for secondary amine while the primary amine was estimated by coupling methylamine with p-nitrodiazonium chloride(57). NH_3 was estimated by indophenol method used by Bolleter et al(58).

3.2.7. Swelling weights.

The swelling weights of the irradiated and unirradiated resins in the sulphate form were measured by the method used by Pepper et al(59).

3.2.8. Weight losses.

The initial weights of all the forms of resins were calculated in the sulphate form, using conversion factors determined experimentally. After irradiation, the capacity measurements were made and the resins chemically converted to the sulphate form, dried at 105°C. to a constant weight and thus the % weight losses of resins were determined.

3.3. Results and Discussion.

3.3.1. Effect of absorbed americium on the radiation stability of the anion exchanger.

In the previous chapter it was shown that the anion complexes such as $Am(SCN)_4^-$, $Am(NO_3)_4^-$ and $AmCl_4^-$ could be absorbed on Deacidite FF and that the distribution coefficients were sufficiently high to enable the alpha-radiolysis of the resin to be conveniently carried out by alpha-particles from the absorbed americium. It was also of interest to study any possible stabilisation against radiolysis of the quaternary ammonium group by presence of an absorbed heavy element.

The decomposition of the thiocyanate and nitrate forms of resin by alpha-particles were therefore studied by absorbing americium as $Am(SCN)_4^-$ and $Am(NO_3)_4^-$ complexes on to the thiocyanate and nitrate forms of resin respectively. A similar study was made by Co-60 γ-radiolysis of the $La(SCN)_4^-$ form of the resin in a slurry of 5M NH_4 SCN.

To distinguish the effect of americium absorbed on the resin functional group from the effect of americium present in close proximity to the group on the radiation stability of the resin, alpha-radiolysis of the NO_3^- resin has also been studied by slurrying the resin in americium solution under conditions such that americium does not go onto the resin.

Studies of γ-radiation induced decomposition of the thiocyanate form of resin slurried in 5M NH_4SCN solution have also been made to compare with γ-radiolysis of $La(SCN)_4^-$ form of resin.

(a) Irradiation of thiocyanate resin by absorbed americium.

NH_4SCN solution was reported to be readily decomposed by radiation to produce sulphur(32, 33). It was therefore necessary to establish that the decomposition of the NH_4SCN in solution was not sufficiently large to disturb the distribution of americium between solution and resin. The γ-radiolysis of 5M NH_4SCN solution showed that the yield of sulphur at 250 megarad was only 3.1% of the total present. When americium is absorbed in the resin as the $Am(SCN)_4^-$ complex from 5M NH_4SCN solution, most of the alpha-particle energy is deposited on the resin and the decomposition of the solution is expected to be comparatively low. It can thus be assumed that not more than 5% of the NH_4SCN will be decomposed by a 500 Mr. alpha-particle dose. Also the fact that the Kd value is of the order of 200, a maximum change of 5% in the concentration of NH_4SCN is not likely to transfer an appreciable amount of americium complex to the solution phase. It was found experimentally that between 160 to 500 Mr., the loss of americium complex from the resin phase to the solution phase, due to the decomposition of NH_4SCN, ranges from 1-5%.

Since the purpose of this work was to find the extent of decomposition of the anion exchange resin by alpha-particles, the possible effects of absorbed americium on the resin and to compare the extent of degradation caused by γ-rays under identical conditions, an alpha dose rate of about 20 Mr. per day was considered appropriate, because a maximum of 19-20 Mr/day of γ-dose could be achieved from the Co-60 source.

Alpha-particle irradiation of the thiocyanate form of resin slurried in 5M NH_4SCN solution was carried out up to 570 Mr. The changes in capacities were estimated by the modified Fisher-Kunin(54) method. Throughout, the standard Fisher-Kunin(53) results are also tabulated, since much of the published work on the radiation stability of anion exchange resin has been based on this method. During the Fisher-Kunin method of estimation, hydrolysis of the strong base occurs to an appreciable extent giving too high a weak base capacity and too low a strong base capacity of the irradiated resin.

As the alpha-particle dose was increased the strong base capacity fell almost linearly up to 200 Mr., while the weak base capacity continued to increase. In the region of 300-500 Mr., the rate of loss of strong base capacity and rise of weak base capacity were much decreased. (Table 3.1. and Fig.3.1.).

Table 3.1 : Alpha particle irradiation of SCN$^-$ form of resin slurried in 5M NH_4SCN : variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction (a) meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	CH_3NH_2 meq/g.	Swelling weight. g.H_2O/g.	% loss in resin weight.
	Weak base.	Strong base.		Weak base.	Strong base.					
Nil	0.46	3.50	0.15	0.31	3.65	Nil	Nil	Nil	0.81	Nil
60	0.95	2.80	0.35	0.60	3.15	0.21	0.027	0.015	0.70	5.10
115	1.10	2.32	0.40	0.70	2.72	0.40	0.028	0.012	0.69	9.30
158	1.46	1.41	0.59	0.87	2.00	0.45	0.099	0.011	-	-
205	1.51	1.65	0.42	1.09	2.07	0.56	0.060	0.009	0.66	10.30
300	1.40	1.32	0.40	1.10	1.72	0.70	0.074	0.032	-	-
368	1.61	0.81	0.52	1.09	1.33	0.84	0.163	0.054	0.57	19.40
570	1.11	0.96	0.20	0.91	1.16	1.10	0.242	0.080	0.44	21.00

All capacities based on initial weights of dry resin in SCN$^-$ form.

Dose rate of 20 Mr/day.

7% of the strong base groups in $Am(SCN)_4^-$ form and

93% of the strong base groups in SCN$^-$ form.

(a) Method of correction explained on page 39.

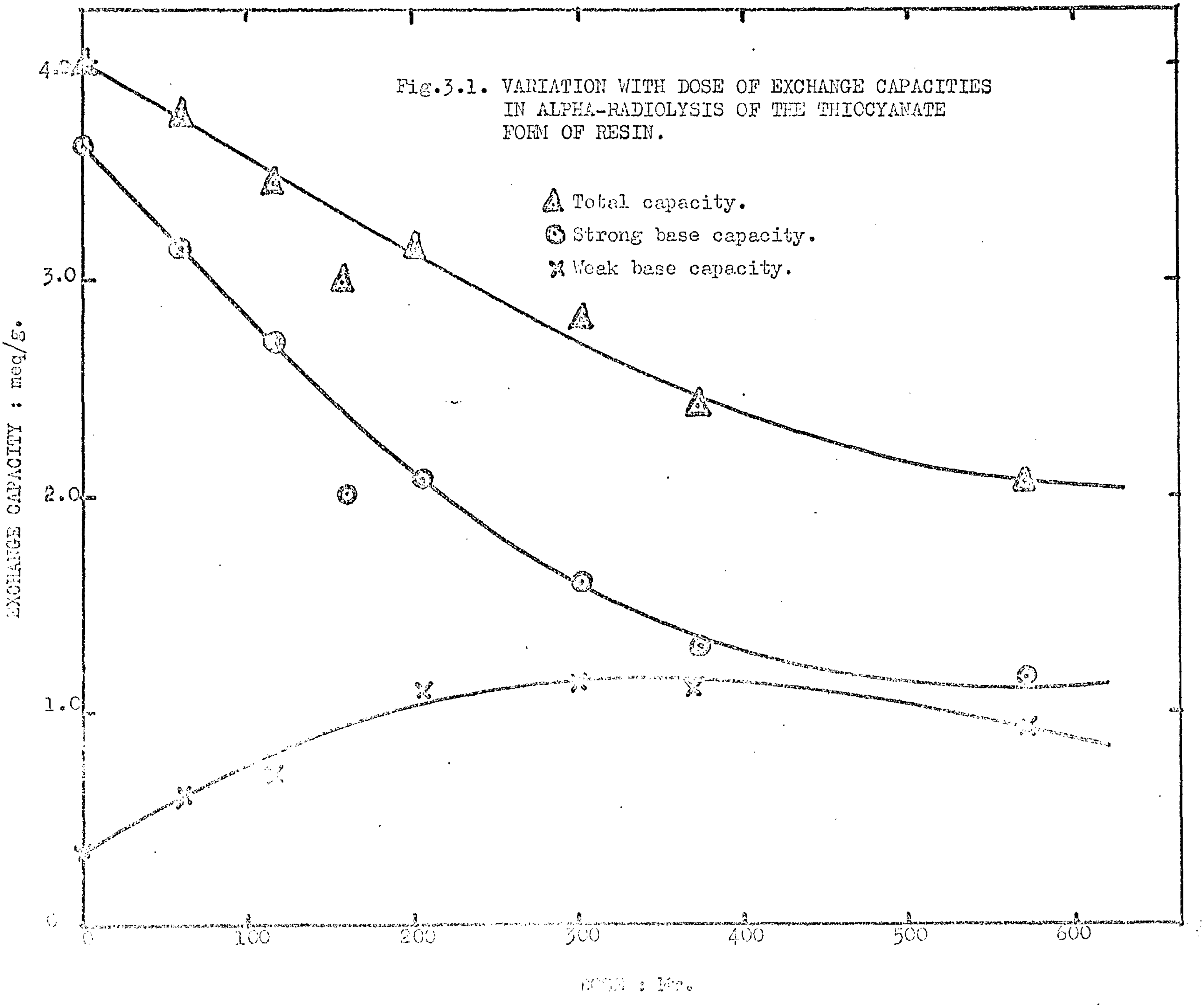


Fig.3.1. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN ALPHA-RADIOLYSIS OF THE THIOCYANATE FORM OF RESIN.

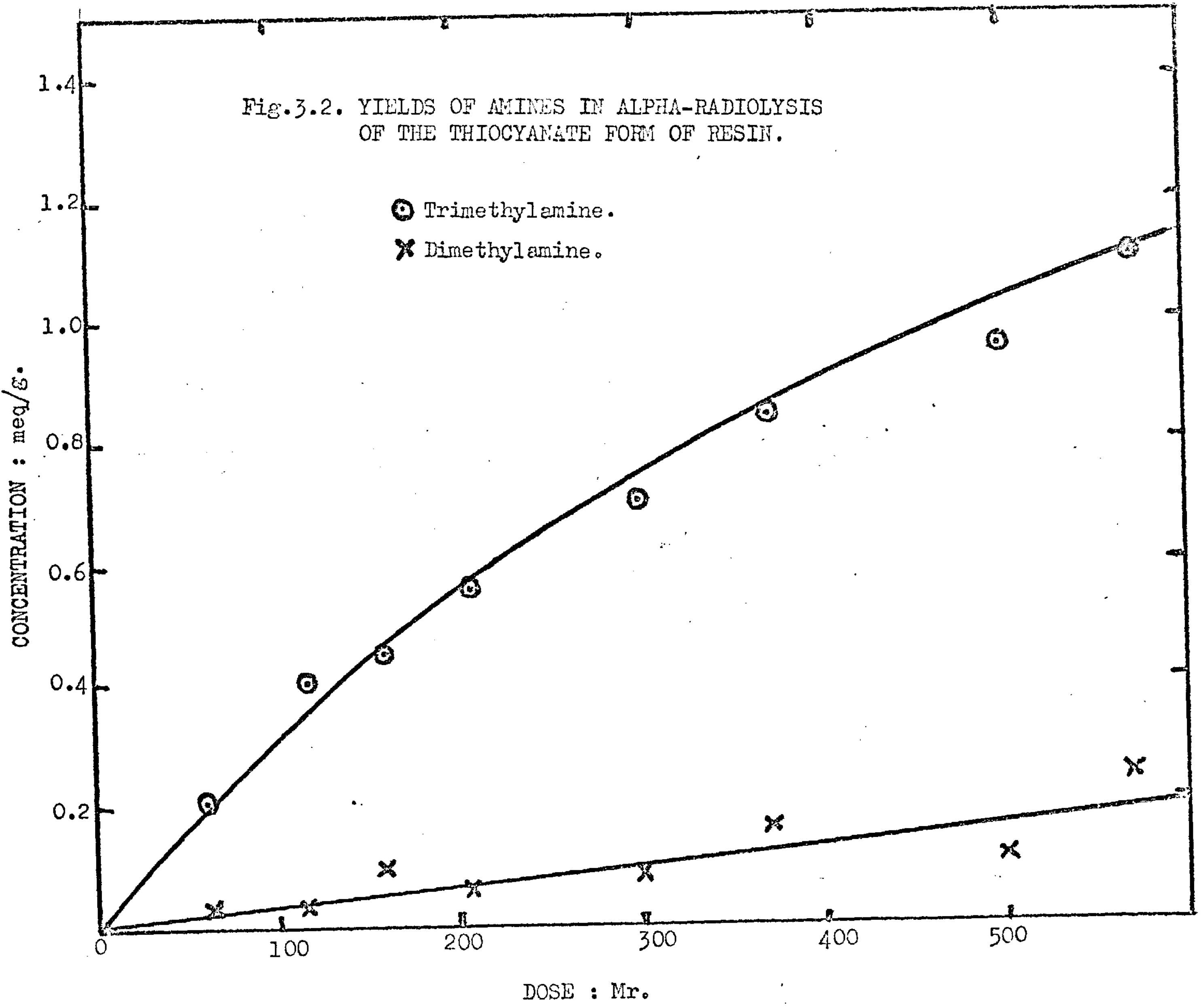


Fig.3.2. YIELDS OF AMINES IN ALPHA-RADIOLYSIS OF THE THIOCYANATE FORM OF RESIN.

These decreased rates could be a consequence of the falling concentration of the functional groups in the resin, as already at 210 Mr., 50% of the strong base groups and 27.5% of the total capacity were lost and consequently an increasingly large part of the energy would be dissipated in the polymer network without breaking off amino groups.

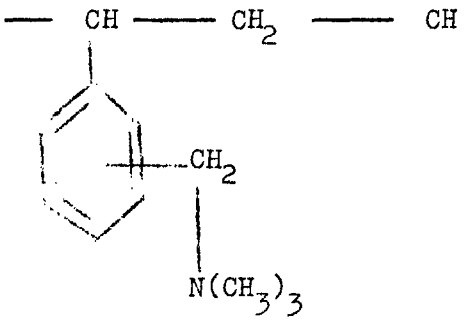
Trimethyl amine was the major product of the radiolytic decomposition of the strong base resin, obviously due to the scission of $C-N(CH_3)_3$ bonds. The formation of weak base groups was brought about by the scission of $N-CH_3$ bonds. Thus the strong base capacity loss was associated with the loss of complete functional groups and conversion to weak base groups by loss of a CH_3 group.

The trimethyl amine yield increased with increase of radiation dose (Table 3.1., Fig.3.2.), but the rate was reduced in the higher dose range presumably because the concentration of the quaternary groups was reduced and secondary radiolytic decomposition of trimethyl amine was greater due to its higher concentration.

The increasing yield ofdimethylamine with increasing dose (Fig.3.2.) **was** due to the decomposition of the weak base functional group, (Fig.3.1.) and radiolytic decomposition of the trimethyl amine (Fig.3.2.). The formation of dimethylamine by the decomposition of weak base functional group was supported by the fall in weak base capacity of the resin in the higher dose range. Creed(17) observed that during the γ-radiolysis of an anion exchange resin in a flowing system, the secondary amine yield was depressed in favour of trimethylamine. Therefore the formation of dimethylamine does not arise entirely from the weak base decomposition, but also secondary decomposition of the trimethylamine must contribute.

Alpha-particle irradiation of the thiocyanate form of resin in 5M NH_4SCN solution caused decrease in the swelling weight with increase of dose (Fig.3.11.). The loss of functional group alone could cause some decrease, but the changes of swelling weight with dose showed that besides the loss of functional groups, crosslinking and possibly de-crosslinking were playing a part. Although functional groups were being decomposed throughout the irradiation, the swelling weight at first decreased and then remained unchanged and finally continued to decrease with dose.

An anion resin such as Deacidite FF could lose more than 45% of its initial weight by complete loss of functional groups. For example, the Cl^- form of Deacidite FF with 8% DVB as crosslinking agent



contains repeating units having monofunctional groups. Taking into account the 8% of DVB, the so-called molecular weight of each unit is 208 and the loss of $(CH_3)_3NCl^-$ from each unit can cause 42% loss in weight. If the resin units are monofunctional, then each g. of dry resin should have 4.5 meq. of functional group and in fact this value was found experimentally. The irradiated resin, as expected, was found to lose weight as functional groups were lost but the losses could not be accounted for completely in this way. It therefore appears that dissolution of polymer network also takes place to some extent in radiolysis of the anion exchange resin. The weight loss increase is rapid up to 300 Mr. and subsequently the rate of loss is considerably reduced. The initial higher rate of weight loss was due to the higher rate of loss of functional groups and solubility of radiolytic polymer fragments. At higher doses the loss of functional groups and solubility decreases, as expected, and it is also possible that less soluble radiolytic polymer fragments are being produced.

In this set of alpha-particle irradiations, the resin was essentially in thiocyanate form with ~7% as $Am(SCN)_4^-$ form. Since the latter groups represented only a small proportion of the total, any effect the americium might have on the stability of the resin could not be seen directly. During alpha-irradiation loss of the strong **base capacity might** be expected to cause some loss of americium from the resin to the solution due to scission of $C\text{-}N^+(CH_3)_3\ Am(SCN)_4^-$ bond. But as the irradiation was carried out in the presence of 5M NH_4SCN solution, the americium redistributed itself between the solution and irradiated resin phase. Thus any attempt to find the extent of $C\text{-}N^+R_3\ Am(SCN)_4^-$ breakage, from the release of americium from the resin to the solution would be a failure.

(b) Irradiation of $La(SCN)_4^-$ and SCN^- forms of resin by γ-rays.

In order to compare the effect of a heavy anion complex on the γ-radiation stability of anion exchange resin, 50% of the SCN^- capacity was converted to the $La(SCN)_4^-$ form and the resin was irradiated in a 5M NH_4SCN slurry, using Co-60 γ-rays. The changes in total and strong base capacities of $La(SCN)_4^-$ form of resin up to a dose of 250 Mr. were somewhat less than those observed for alpha-radiolysis of the thiocyanate form of resin. Above 250 Mr., both γ and alpha-radiolysis followed the same pattern. γ-radiolysis caused 50% loss of the strong base capacity and 37.5% loss of total capacity at 260 Mr. (Fig.3.3.). Although 50% loss of the strong base capacity occurred almost at the same dose by both alpha-particle and γ-rays, the essential difference was that γ-radiation caused comparatively more breakdown of $C-N^+R_3$ bonds (37.5%) and less of $^+N-CH_3$ groups (12.5%) whereas alpha-particles caused 27.5% breakage $C-N^+R_3$ bonds and 23.5% of $^+N-CH_3$ bonds at the same dose. This is also evident from the fact that the maximum rise in weak base capacity in the former case was only 0.45 meq/g. compared to 0.8 meq/g. in the latter.

The gamma radiolysis of thiocyanate form of resin has been carried out under the same conditions as alpha radiolysis of the resin and gamma radiolysis of the $La(SCN)_4^-$ form of resin, i.e. in 5M NH_4SCN solution.

Fig.3.5. shows that the capacity losses due to γ-irradiation followed the same pattern as alpha-particle irradiation of the resin. 50% of the strong base and 32.5% of the total capacities were lost at 285 Mr. Here again, γ-radiolysis of the SCN^- form caused a higher ratio of $C-NR_3$: $N-CH_3$ bond breakage. Table 3.6. shows that alpha-radiolysis caused somewhat less total damage than γ-radiolysis of the same resin.

The trimethylamine yields increased with increase of radiation doses in all cases. But at a fixed dose, say 300 Mr. (Fig.3.2., 3.4., 3.6.) alpha-radiolysis of SCN^- resin, γ-radiolysis of $La(SCN)_4^-$ and SCN^- resins produced 0.74, 1.5 and 1.3 meq/g. of trimethylamine respectively. This was again in agreement with the conclusion drawn from capacity changes that alpha-particle caused less scission of $C-NR_3$ bond than γ-radiation.

Table 3.2 : Gamma irradiation of $La(SCN)_4^-$ form of resin slurried in 5M NH_4SCN : variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction	Corrected capacities. meq/g.		$(CH_3)_3N$	$(CH_3)_2NH$	Swelling weight.	% loss in resin weights.
	Weak base.	Strong base.	meq/g.	Weak base.	Strong base.	meq/g.	meq/g.	g.H_2O/g.	
Nil	0.87	3.13	0.41	0.46	3.59	Nil	Nil	0.82	Nil
130	1.12	2.35	0.40	0.72	2.75	0.72	0.046	0.63	7.55
2.35	1.48	1.35	0.61	0.87	1.96	1.21	0.116	0.69	10.00
330	1.24	0.71	0.43	0.81	1.14	1.64	0.160	0.53	13.85
500	1.16	0.51	0.26	0.90	0.77	1.82	0.196	0.39	17.25

All capacities based on initial weights of dry resin in SCN^- form.

(a) Dose rate of 20 Mr/day.
(b) 50% of the strong base groups in $La(SCN)_4^-$ form.

Table 3.3 : Gamma irradiation of SCN^- form of resin slurried in 5M NH_4SCN : variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities. meq/g.		Capacity correction.	Corrected capacities meq/g.		$(CH_3)_3N$	$(CH_3)_2NH$	CH_3NH_2	Swelling weights	% loss in resin weights.
	Weak base.	Strong base.	meq/g.	Weak base.	Strong base.	meq/g.	meq/g.	meq/g.	g.H_2O/g.	
Nil	0.65	3.30	0.30	0.35	3.60	Nil	Nil	Nil	0.81	Nil
43	0.82	2.86	0.39	0.43	3.25	0.31	0.02	0.009	-	5.80
100	0.93	2.40	0.48	0.45	2.88	0.45	0.04	0.008	0.51	10.10
141	1.04	2.14	0.41	0.63	2.55	0.72	0.07	0.009	0.56	10.60
295	1.31	1.16	0.30	1.01	1.46	1.27	0.13	0.021	0.53	13.60
505	1.69	0.83	0.36	1.33	1.19	1.14	0.12	0.023	0.44	20.30

Dose rate of 20 Mr/day.

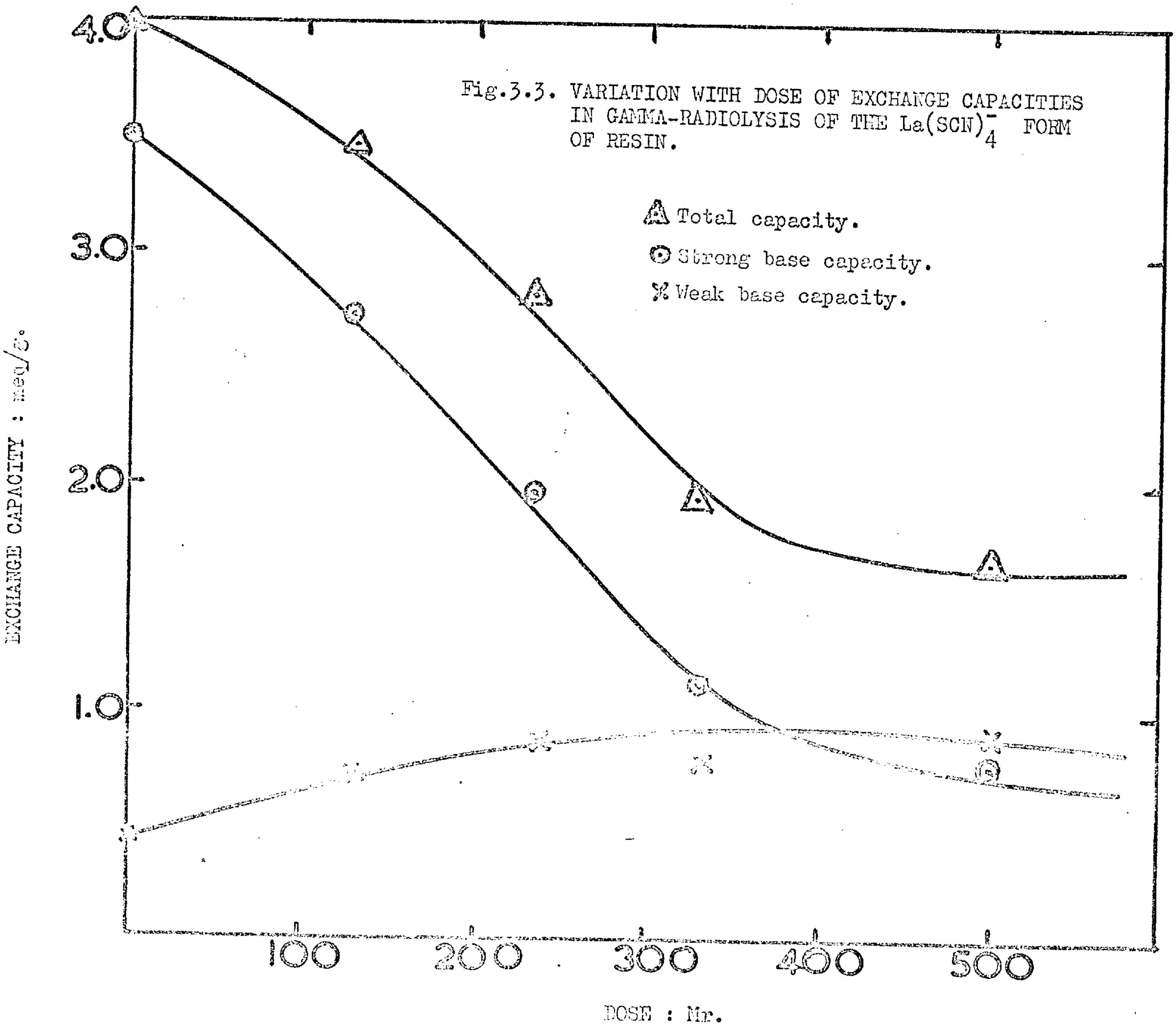


Fig.3.3. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN GAMMA-RADIOLYSIS OF THE $La(SCN)_4^-$ FORM OF RESIN.

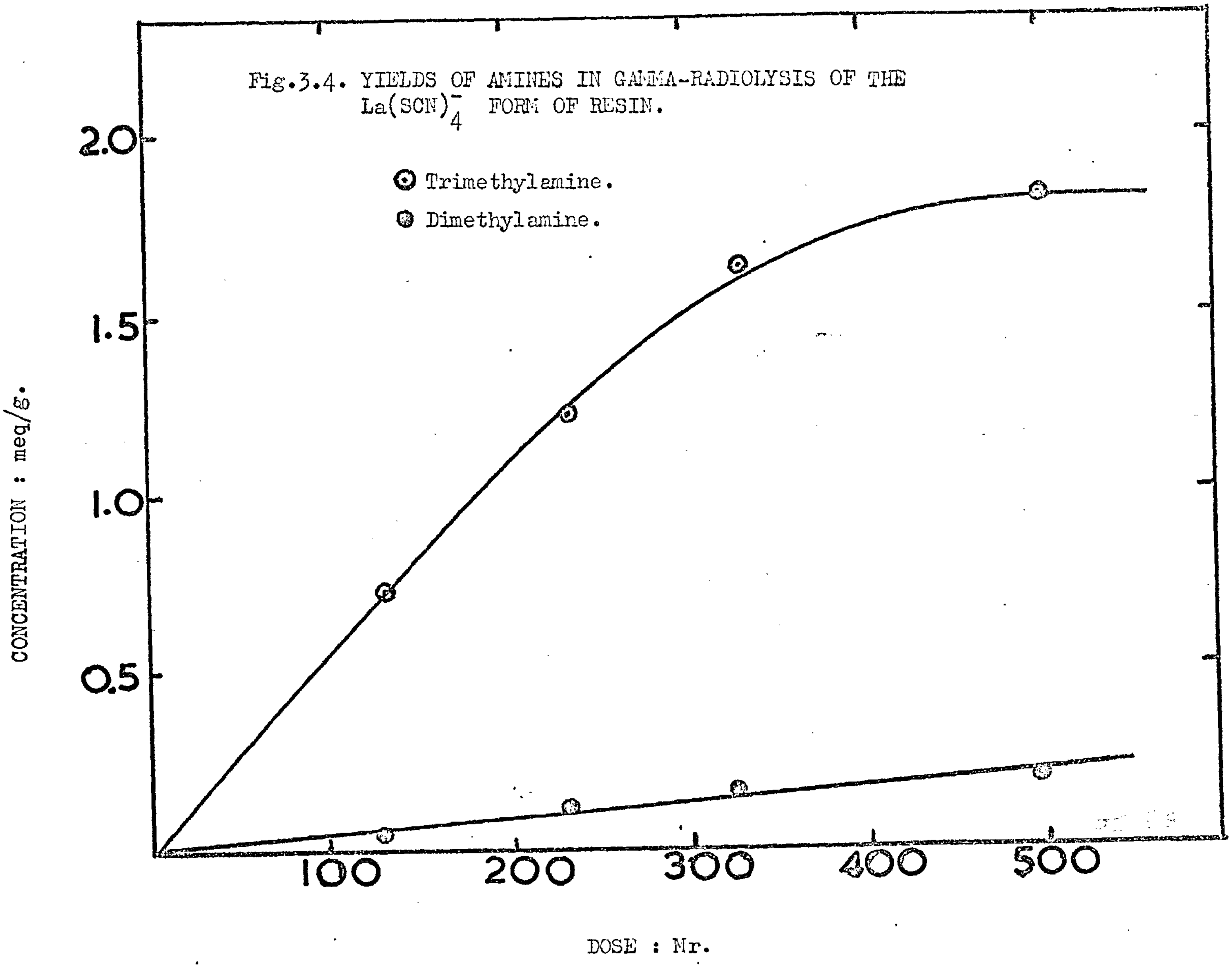


Fig.3.4. YIELDS OF AMINES IN GAMMA-RADIOLYSIS OF THE $La(SCN)_4^-$ FORM OF RESIN.

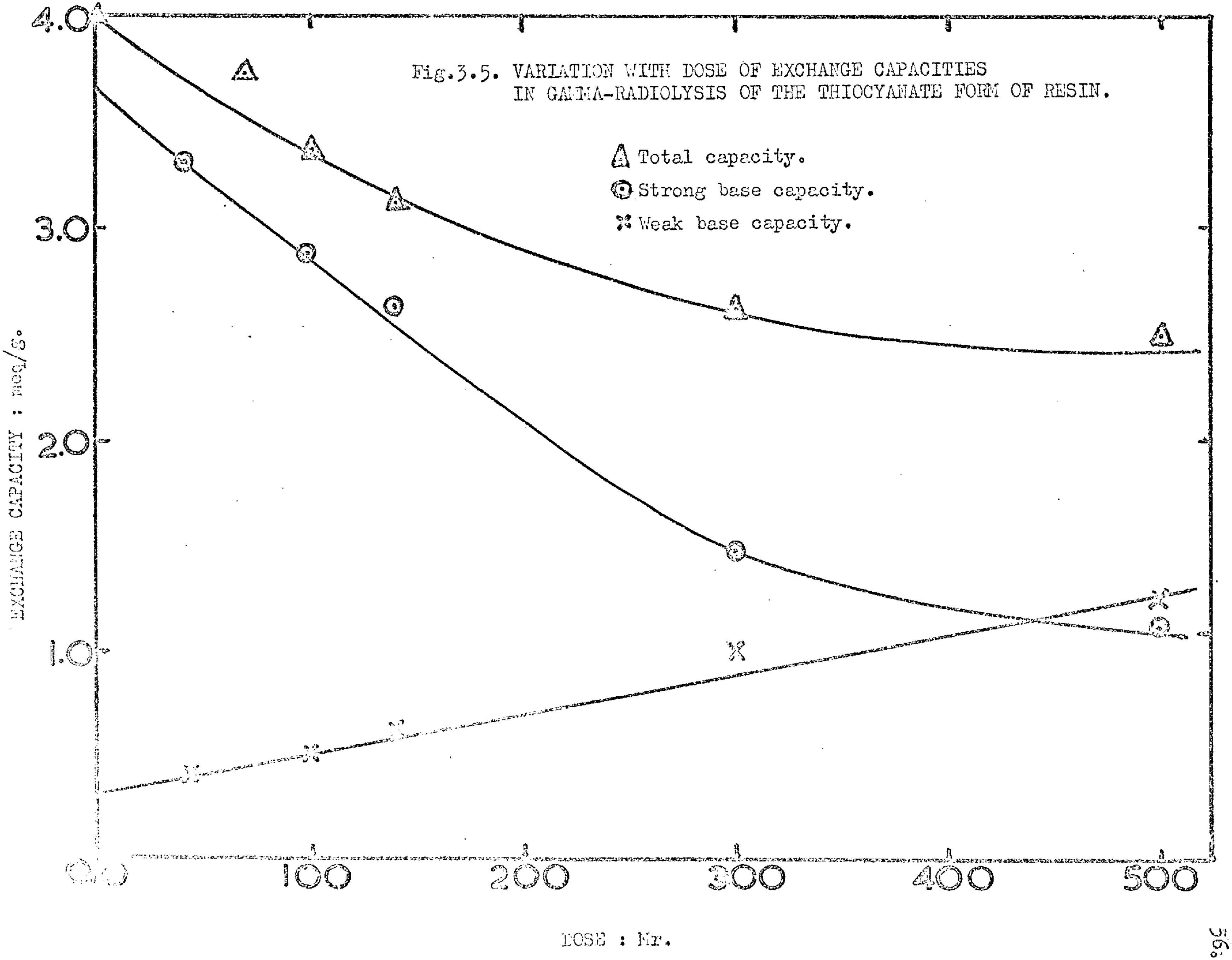


Fig.3.5. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN GAMMA-RADIOLYSIS OF THE THIOCYANATE FORM OF RESIN.

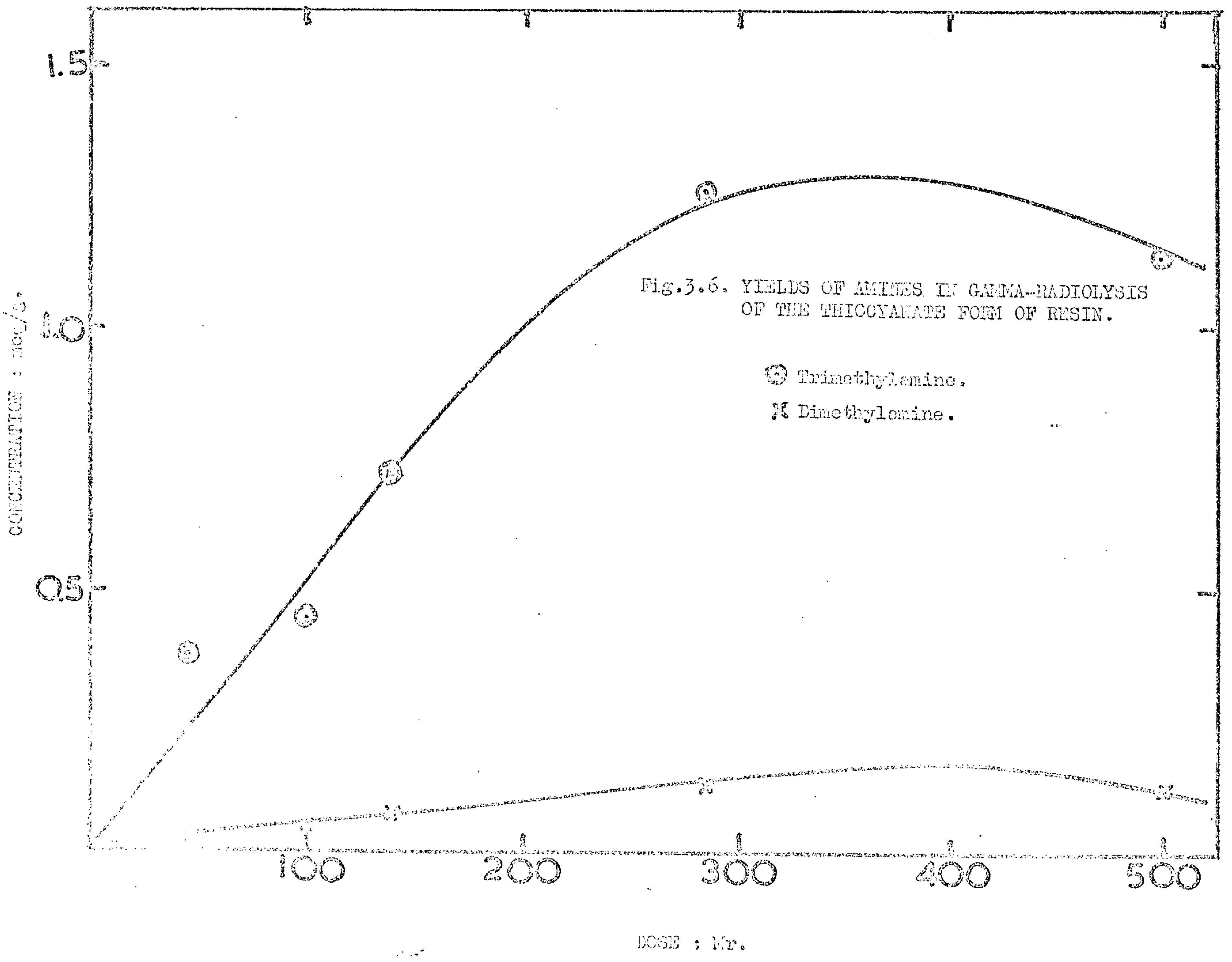


Fig.3.6. YIELDS OF AMINES IN GAMMA-RADIOLYSIS OF THE THIOCYANATE FORM OF RESIN.

At 500 Mr. the extent of $N(CH_3)_3$ production was low in all cases due to lower concentration of functional groups. At higher doses in γ-radiolysis there was in fact a nett destruction due to the fact that the rate of production of $N(CH_3)_3$ was much slower than the rate of disappearance due to secondary radiolysis.

The yield of $(CH_3)_2NH$ also increased with increasing radiation dose in all the three cases. The yields of dimethylamine at 300 Mr. for alpha-radiolysis of thiocyanate form and γ-radiolysis of $La(SCN)_4^-$ and thiocyanate forms are 0.10, 0.13 and 0.14 meq/g. respectively. The somewhat lower yield of dimethylamine in alpha-radiolysis may be due to the smaller secondary decomposition of trimethylamine by alpha-particles.

The irradiations of SCN^- form of resin in 5M NH_4SCN might have been complicated by secondary decomposition of NH_4SCN solution producing CN radicals. These complications can be avoided by using a simpler system, e.g. resin irradiated with americium solution in a dilute acid. But it was necessary to establish whether the extent of alpha-particle radiation damage was dependent on whether or not the americium was absorbed on the resin.

(c) Irradiation of NO_3^- resin by absorbed americium and by americium solution.

The nitrate form of resin was irradiated with alpha-particles by absorption of the nitrate complex of americium on the resin from 8M $LiNO_3$ solution in 0.05M HNO_3 and also by slurrying the resin with americium nitrate solution in 0.005M HNO_3. In both cases, the resin became darker with increase of alpha dose and gas bubbles were formed within the resin slurries.

An examination of Fig.3.7. and 3.9. shows that alpha-radiolyses of nitrate resin under the two circumstances mentioned above degrade the resin in a similar manner. In the case of the absorbed americium complex in the resin, 50% of the strong base and 25% of the total capacities were lost at 600 Mr. and thus scission of $C-\overset{+}{N}(CH_3)_3$ and $\overset{+}{N}-CH_3$ bond is equal in extent. The alpha-particle irradiation with slurried americium solution showed that 45% of the strong base and 30% of the total capacities were degraded by 600 Mr. In this case, scission of $C-\overset{+}{N}(CH_3)_3$ bond proceeds at a higher rate than the scission of $\overset{+}{N}-CH_3$ bond and thus producing less weak base **groups**. This was also apparent in the trimethylamine yields.

It was also noted that although the production of weak base capacity **in the latter case** was less than the absorbed americium-resin system, the dimethylamine yield was higher. This showed that dimethylamine was essentially the radiolytic decomposition product of trimethylamine. The **G-values** for loss of total **capa**cities and production of weak base by the first 100 Mr. var**y** due to difference in the courses of reactions in the two cases, although the -G strong base capacity were almost the same. (Table 3.6.).

Table 3.4 : Alpha particle irradiation of NO_3^- form of resin in 0.05N HNO_3 : variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction. meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	Swelling weights. g.H_2O/g.	% loss in resin weights.
	Weak base.	Strong base.		Weak base.	Strong base.				
Nil	0.27	3.82	0.22	0.05	4.04	Nil	Nil	0.82	Nil
314	0.91	2.51	0.32	0.59	2.83	0.67	0.038	1.29	16.50
470	1.44	1.60	0.76	0.68	2.36	0.85	0.029	1.38	19.50
730	1.22	1.42	0.44	0.78	1.85	1.16	0.060	1.46	23.00
925	1.38	1.00	0.54	0.84	1.54	1.26	0.051	1.57	26.50
1258	1.63	0.56	0.54	1.09	1.10	1.38	0.111	1.73	30.00

Dose rate of 20 Mr/day.

7% of the strong base groups in $Am(NO_3)_4^-$ form and
93% of the strong base groups in NO_3^- form.

Table 3.5 : Alpha particle irradiation of NO_3^- form of resin in 0.005N HNO_3 : variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	Swelling weights. meq/g.	% loss in resin weights.
	Weak base.	Strong base.		Weak base.	Strong base.				
Nil	0.25	3.88	0.19	0.06	4.07	Nil	Nil	0.81	Nil
102	0.40	3.30	0.24	0.16	3.54	0.26	0.030	1.08	8.0
184	0.54	2.96	0.36	0.18	3.32	0.52	0.036	1.00	10.0
303	1.22	2.45	0.55	0.67	3.00	0.72	0.043	1.25	16.5
386	1.04	1.99	0.58	0.46	2.57	0.83	0.072	1.28	19.0
505	1.55	1.48	1.00	0.55	2.48	1.02	0.079	1.30	20.0

Dose rate of 10 Mr/day.

Nitrate resin slurried with $Am(NO_3)_3$ solution in approximately 0.005N HNO_3.

TABLE 3.6.

G-values **for** the decomposition of resins.

Form of resin	Radiation	Dose Mr.	-G total capacity.	-G SB capa-city.	+G WB capa-city.
SCN^- in 5M NH_4SCN.	alpha-particle	100	4.1	8.2	4.1
		500	3.66	4.8	1.3
$LaSCN^-$ in 5M NH_4SCN	γ-ray	100	3.8	5.3	1.93
		500	4.8	5.3	0.96
SCN^- in 5M NH_4SCN	γ-ray	100	6.0	7.9	1.93
		500	2.9	4.9	1.93
NO_3^- resin with absorbed americium complex.	alpha-particle	100	2.2	4.1	2.0
		500	2.1	3.5	1.4
NO_3^- resin with americium in slurry	alpha-particle	100	2.7	4.1	1.5
		500	2.2	3.2	1.1

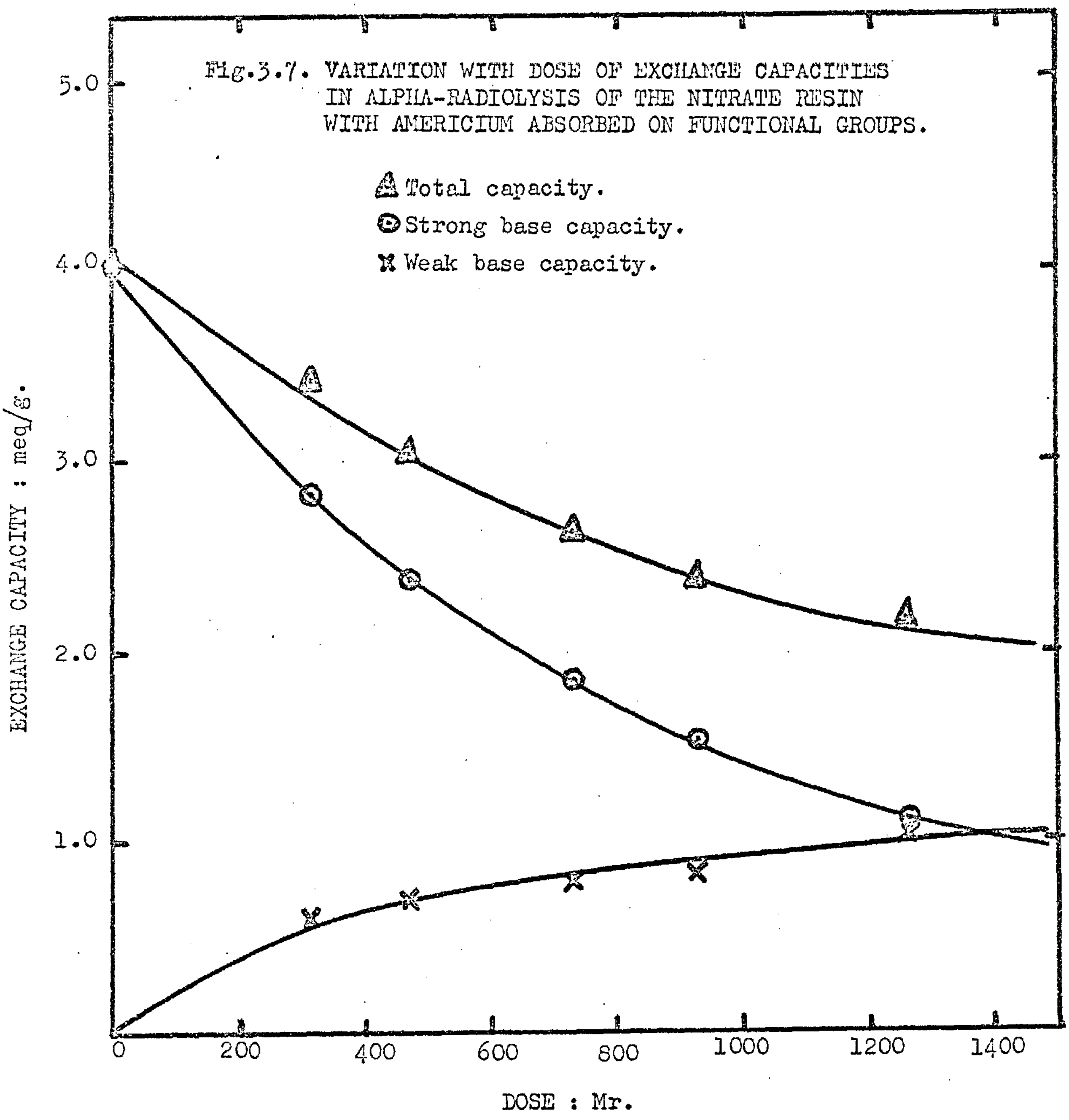


Fig.3.7. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN ALPHA-RADIOLYSIS OF THE NITRATE RESIN WITH AMERICIUM ABSORBED ON FUNCTIONAL GROUPS.

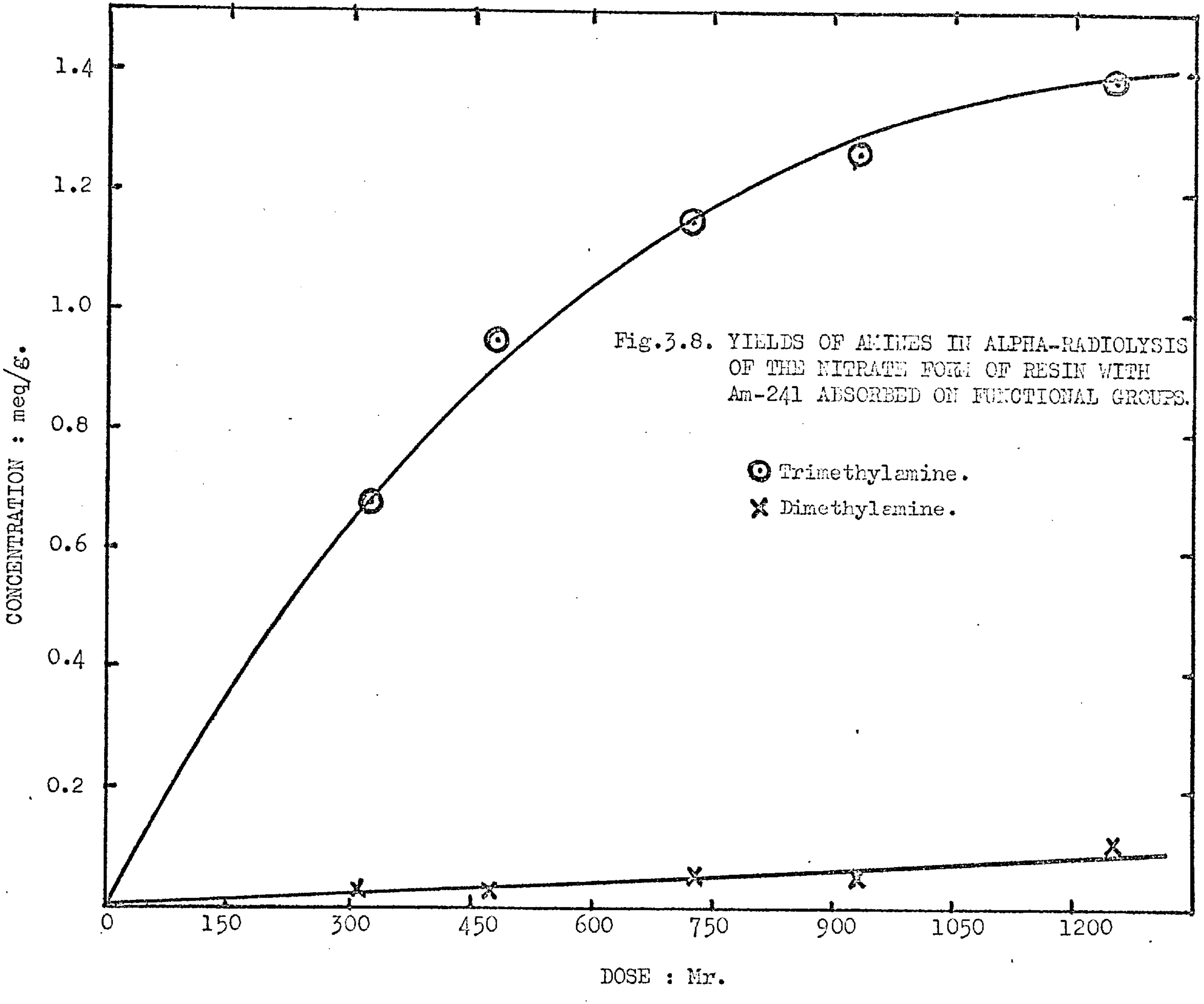


Fig.3.8. YIELDS OF AMINES IN ALPHA-RADIOLYSIS OF THE NITRATE FORM OF RESIN WITH Am-241 ABSORBED ON FUNCTIONAL GROUPS.

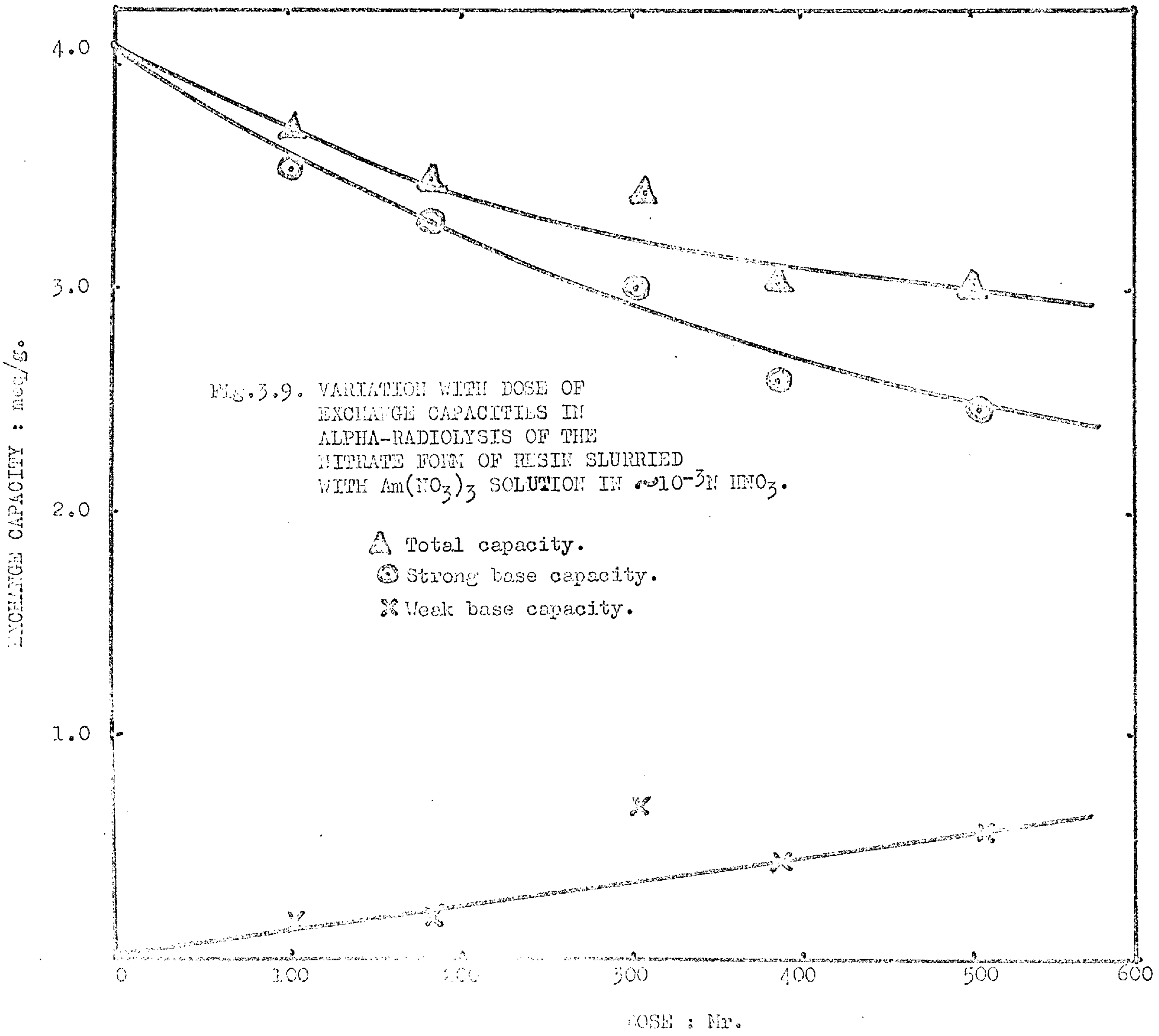


Fig.3.9. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN ALPHA-RADIOLYSIS OF THE NITRATE FORM OF RESIN SLURRIED WITH $Am(NO_3)_3$ SOLUTION IN $\sim 10^{-3}$N HNO_3.

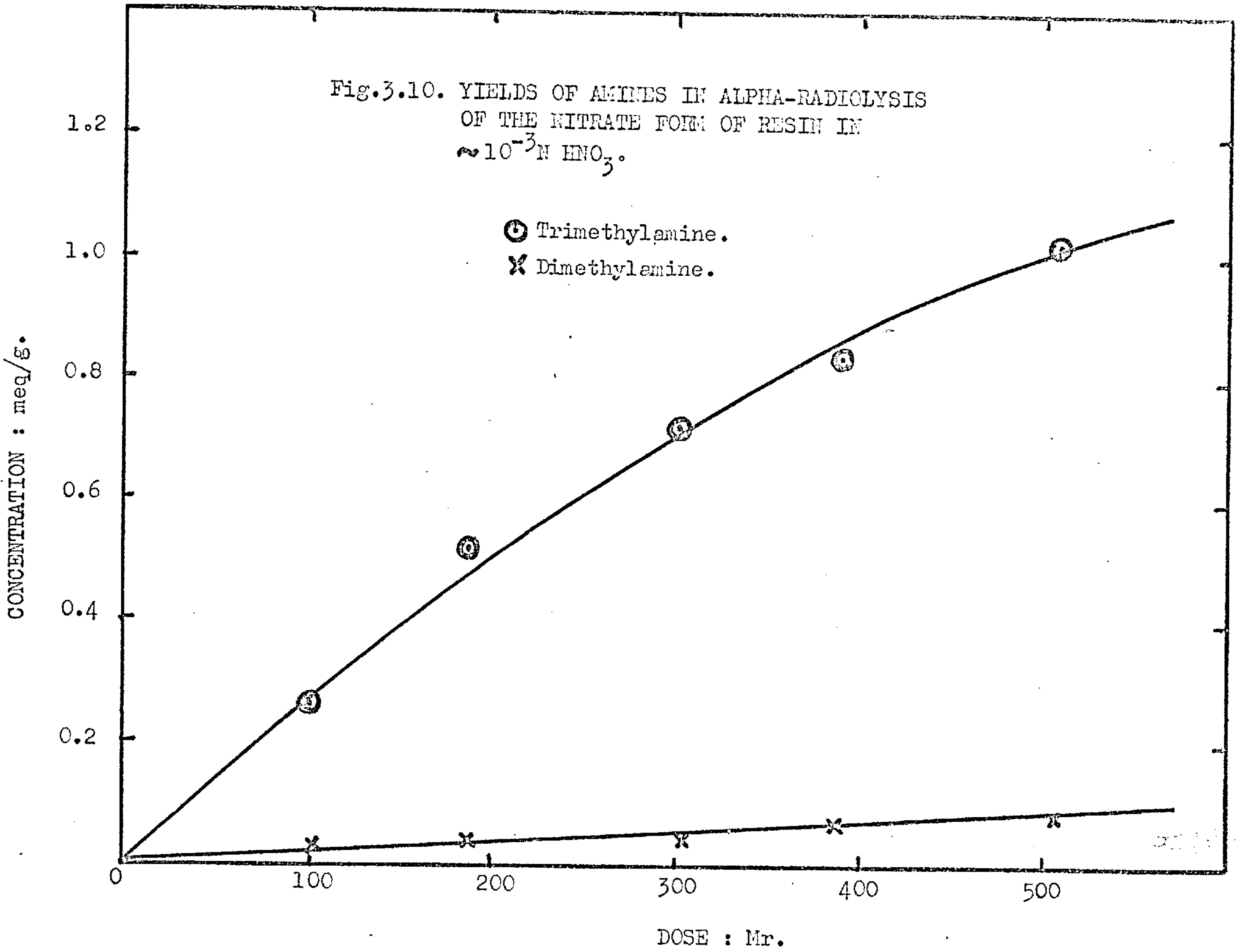


Fig.3.10. YIELDS OF AMINES IN ALPHA-RADIOLYSIS OF THE NITRATE FORM OF RESIN IN $\sim 10^{-3}$N HNO_3.

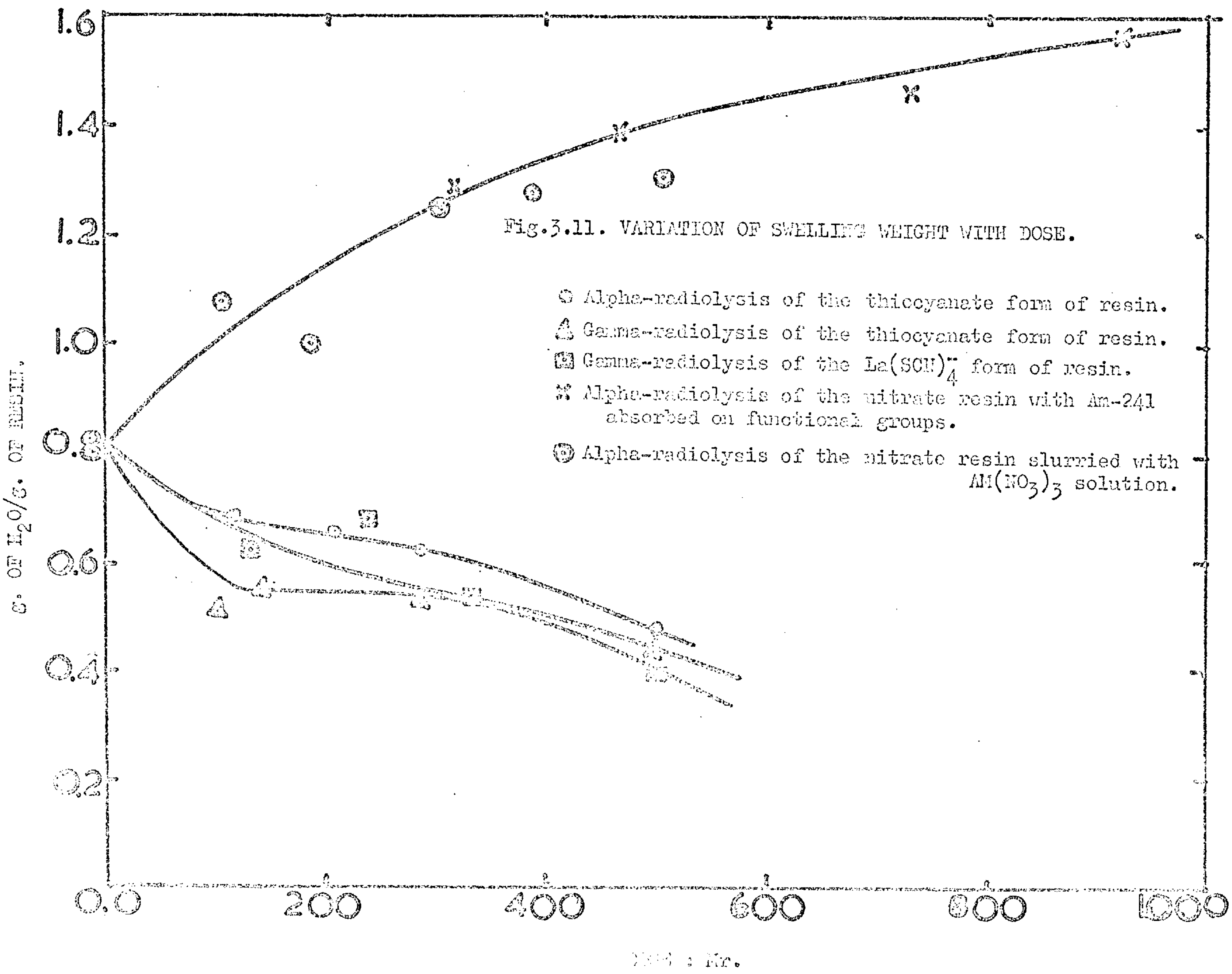


Fig.3.11. VARIATION OF SWELLING WEIGHT WITH DOSE.

At 500 Mr. resin decompositions were the same, -G total being almost twice the value of +GWB. It is found, therefore, that at higher doses, loss of strong base capacity was the same whether americium was absorbed on the resin or merely present in the slurrying solution.

The changes in swelling weights of the irradiated resins with increasing dose differed from those observed in γ and alpha-radiolysis of the SCN^- form of resin in 5M NH_4SCN in that the swelling weight increased rather than decreased. At 1000 Mr., 42% of the total capacity and 65% of strong base capacity were lost and some decrease in swelling weight could normally be expected. The swelling weight, however, was twice the original value, indicating that decrosslinking is an important phenomenon during alpha-irradiation. (Fig.3.11.).

It may be concluded that γ-radiolysis of the anion exchange resin caused more damage than alpha-radiolysis. Fixation of a heavy element as an anion complex, i.e. $La(SCN)_4^-$, to the resin was found not to result in an increased radiation stability. The differences in alpha-radiolyses of $(SCN)^-$ and NO_3^- forms could be due to the additional complication of the presence of 5M NH_4SCN solution in the former case.

3.3.2. Radiation stabilities of the different anionic forms of the resins.

In the previous section 3.3.1., radiolyses of the nitrate and thiocyanate forms of the resins were discussed. It was shown that satisfactory irradiations could be carried out with the americium dissolved in the slurrying solution and this method of α-radiolysis provides a method for studying the relative stabilities of the different anionic forms of resins and also a direct comparison with γ-radiolysis of the same forms of resin. This section is therefore concerned with alpha and gamma radiation damage of different anionic forms of resins; alpha particle irradiations of chloride and sulphate forms being carried out by slurrying the resin with americium solution in the appropriate acid and gamma irradiations on chloride, sulphate and phosphate forms **in** aqueous slurry.

Capacity changes:

(a) Alpha radiolysis of the chloride and the sulphate forms of resins.

The capacity changes due to the alpha radiolysis of the chloride and sulphate forms of resins are given (Table 3.7. and 3.8.). An examination of Figs.3.12. and 3.14. shows that with increasing alpha radiation dose, there is an increasing loss of functional groups and conversion of strong base groups to weak base groups. Thus the total capacity and the strong base capacity decreased while the weak base capacity increased with increase of dose. It can be seen (Fig.3.12.) that the decomposition of the strong base groups of the chloride form of resin is linear with alpha radiation dose at least up to 500 Mr., the total capacity however changes to a lesser extent due to the contribution of weak base groups at doses above about 200 Mr. The strong base and the total capacities of the sulphate form of the resin decreased exponentially with the increasing dose (Fig.3.14.).

The chloride form of resin has lost 50% of the strong base capacity and 36.5% of the total capacity at 465 Mr. Similarly, at 500 Mr., the sulphate form of resin has lost 50% of the strong base capacity and 35% of the total capacity. However, it may be mentioned that the relative stabilities of the different forms of resins cannot strictly be measured from the dose required to bring about 50% of the strong base capacity change of a resin, except when resins with the same initial concentration of the functional groups are used. Another way of comparing the stabilities of the different forms of the resins is to compare the G-values for decomposition of strong base and total capacities and for production of weak base capacities. In this work the resin stabilities are discussed with reference to both the half value dose and to the G-values at 100 Mr. and 500 Mr. doses. Table 3.12. shows that G-values for loss of total capacity of the sulphate form of resin at both 100 and 500 Mr. are less than those for the chloride form of resin. This is possibly a consequence of the difference in concentrations of the functional groups in the resin, i.e. the total capacities of chloride and sulphate forms initially are 4.55 and 3.35, respectively. It is also noted that in the chloride form of resin, G-strong base capacity did not change with increase of dose up to 500 Mr., although change in G-total capacity were noted. This is because of the considerable growth of weak base capacity in the chloride form of resin. This substantial increase in weak base capacity at high doses was not noted in the α-radiolysis of the sulphate form of the resin. However, it may be noted that the alpha radiolysis of the sulphate form of resin was carried out in presence of 0.6N H_2SO_4 while the chloride form in presence of 10^{-3}NHCl. The effect of the hydrogen ion concentration will be discussed in the next section.

Table 3.7 : Alpha particle irradiation of chloride form of resin in approximately 10^{-3}NHCl : variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction.	Corrected capacities meq/g.		$(CH_3)_3N$	$(CH_3)_2NH$	Swelling weights	% loss in resin weights.
	Weak base.	Strong base.	meq/g.	Weak base.	Strong base.	meq/g.	meq/g.	$g.H_2O/g$	
Nil	0.39	4.19	0.31	0.08	4.50	Nil	Nil	0.82	Nil
83	0.84	3.12	0.74	0.10	3.86	0.34	0.055	1.09	6.0
200	1.36	2.28	1.22	0.14	3.50	0.73	0.125	1.17	11.0
396	0.82	2.33	0.39	0.43	2.71	1.33	0.182	1.30	19.0
462	1.30	1.73	0.77	0.53	2.50	1.38	0.200	1.34	20.5
500	1.17	1.55	0.54	0.63	2.09	1.50	0.230	1.52	23.0

Dose rate of 10 Mr/day.
Chloride form of resin slurried with $AmCl_3$ solution in ~10^{-3}N HCl.

Table 3.8 : Alpha particle irradiation of sulphate form of resin in $0.6NH_2SO_4$: variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction.	Corrected capacities meq/g.		$(CH_3)_3N$	$(CH_3)_2NH$	CH_3NH_2	NH_3	Total volatile base.	Swelling weights	% loss in resin weights.
	Weak base.	Strong base.	meq/g.	Weak base.	Strong base.	meq/g.	meq/g.	meq/g.	meq/g.	meq/g.	gH_2O/g	
Nil	0.76	2.60	0.30	0.46	2.90	Nil	Nil	Nil	Nil	Nil	0.81	Nil
152	1.05	1.74	0.48	0.57	2.22	0.42	0.08	0.027	Nil	0.46	1.13	8.5
254	1.10	1.36	0.54	0.56	1.90	0.66	0.12	0.039	Nil	0.72	1.12	14.0
335	1.11	1.24	0.50	0.62	1.74	0.85	0.13	0.034	Nil	1.04	1.00	15.0
385	1.05	1.22	0.44	0.62	1.66	0.89	0.15	0.039	Nil	1.08	0.94	16.0
505	1.03	1.12	0.30	0.73	1.42	1.04	0.14	0.050	Nil	1.21	1.07	18.0

Dose rate of 20 Mr/day.

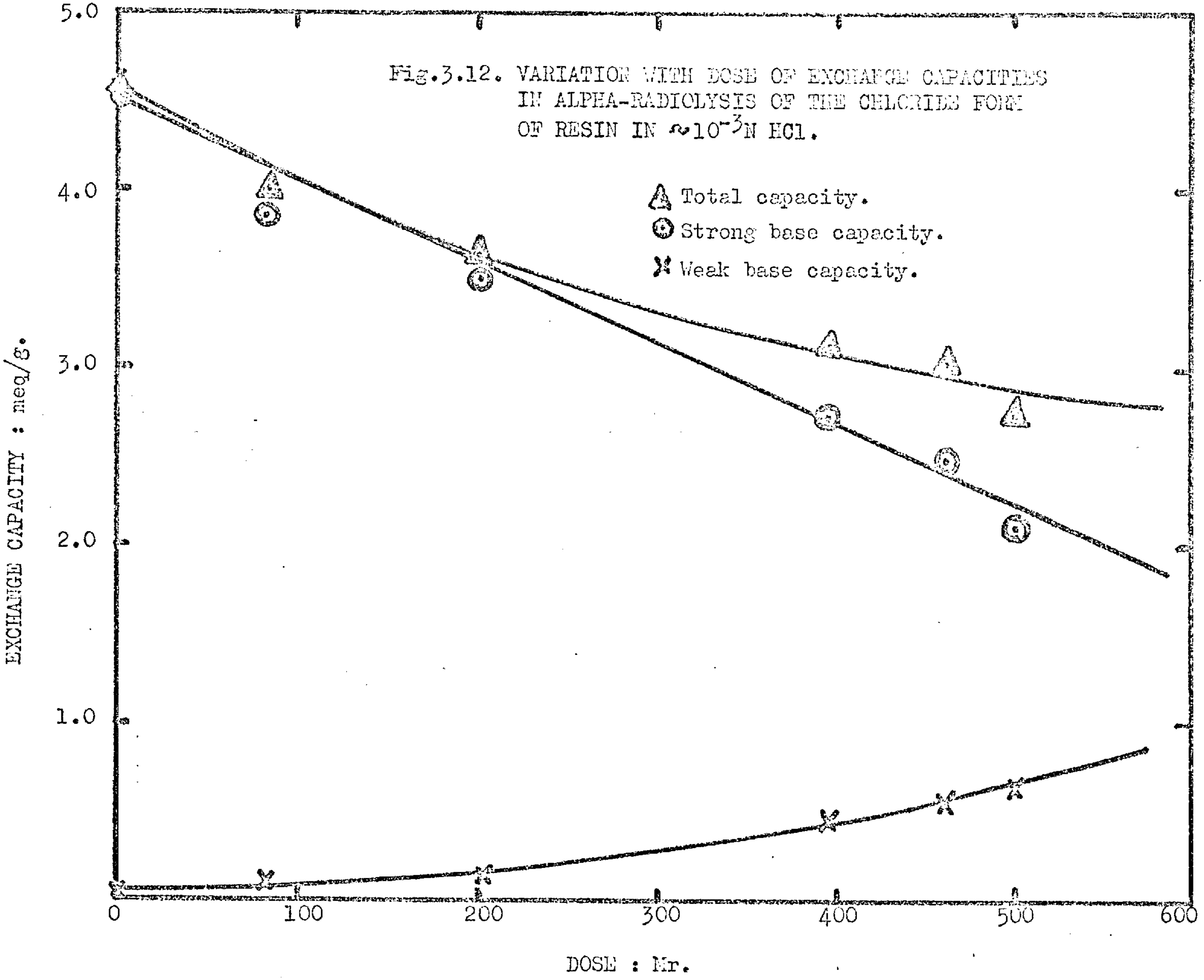


Fig.3.12. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN ALPHA-RADIOLYSIS OF THE CHLORIDE FORM OF RESIN IN $\sim 10^{-3}$N HCl.

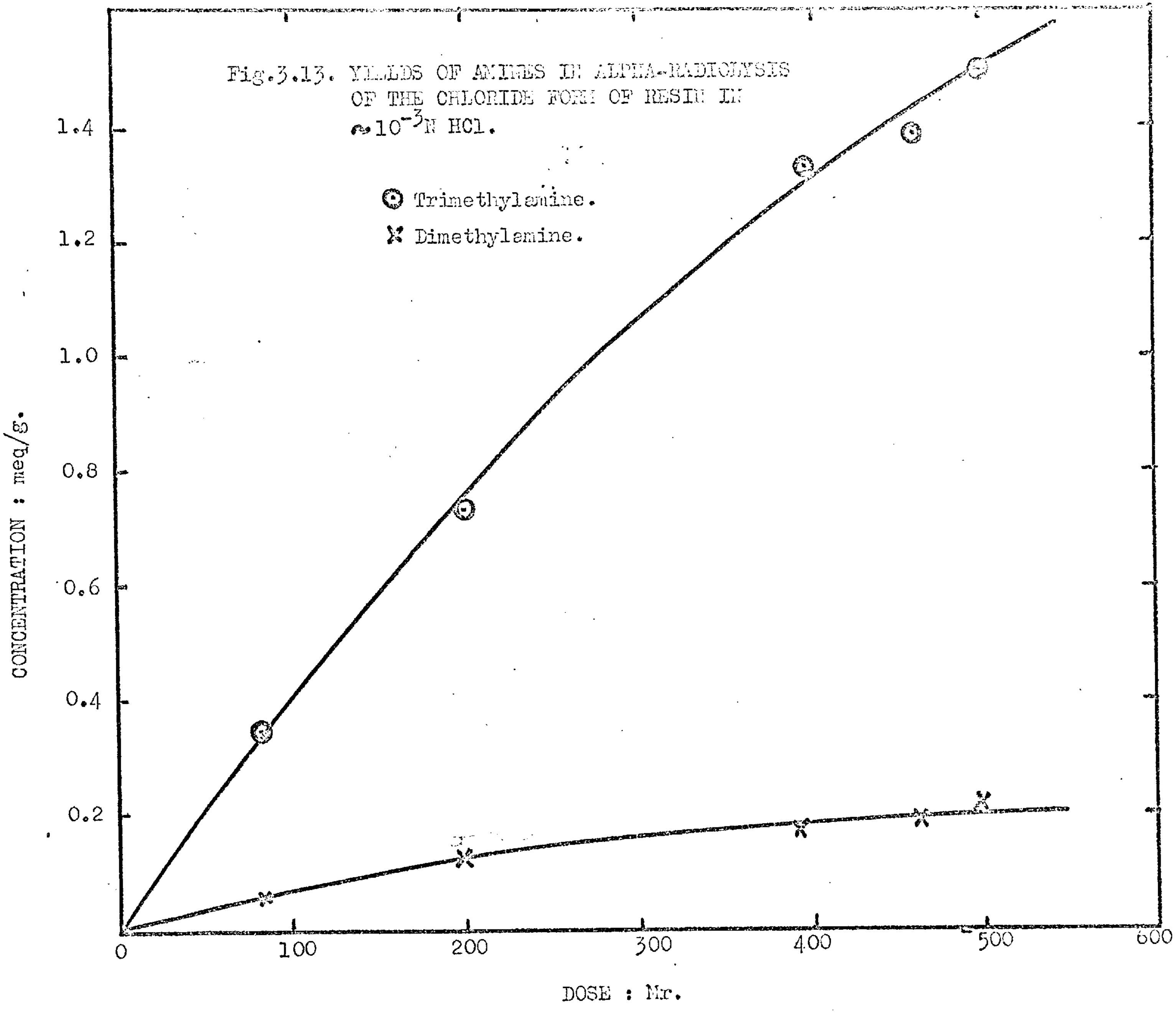


Fig.3.13. YIELDS OF AMINES IN ALPHA-RADIOLYSIS OF THE CHLORIDE FORM OF RESIN IN $\sim 10^{-3}$ N HCl.

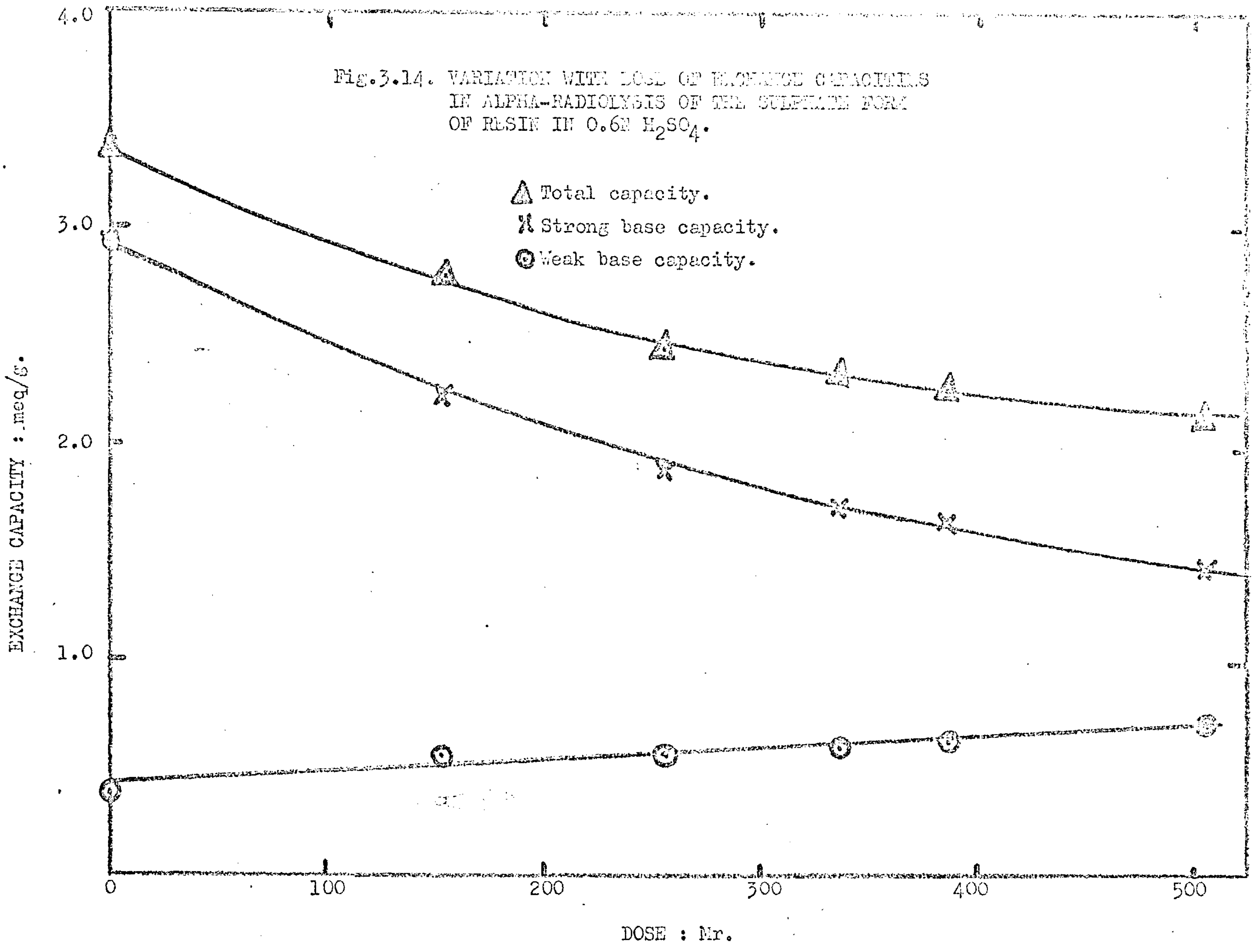


Fig.3.14. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN ALPHA-RADIOLYSIS OF THE SULPHATE FORM OF RESIN IN 0.6N H_2SO_4.

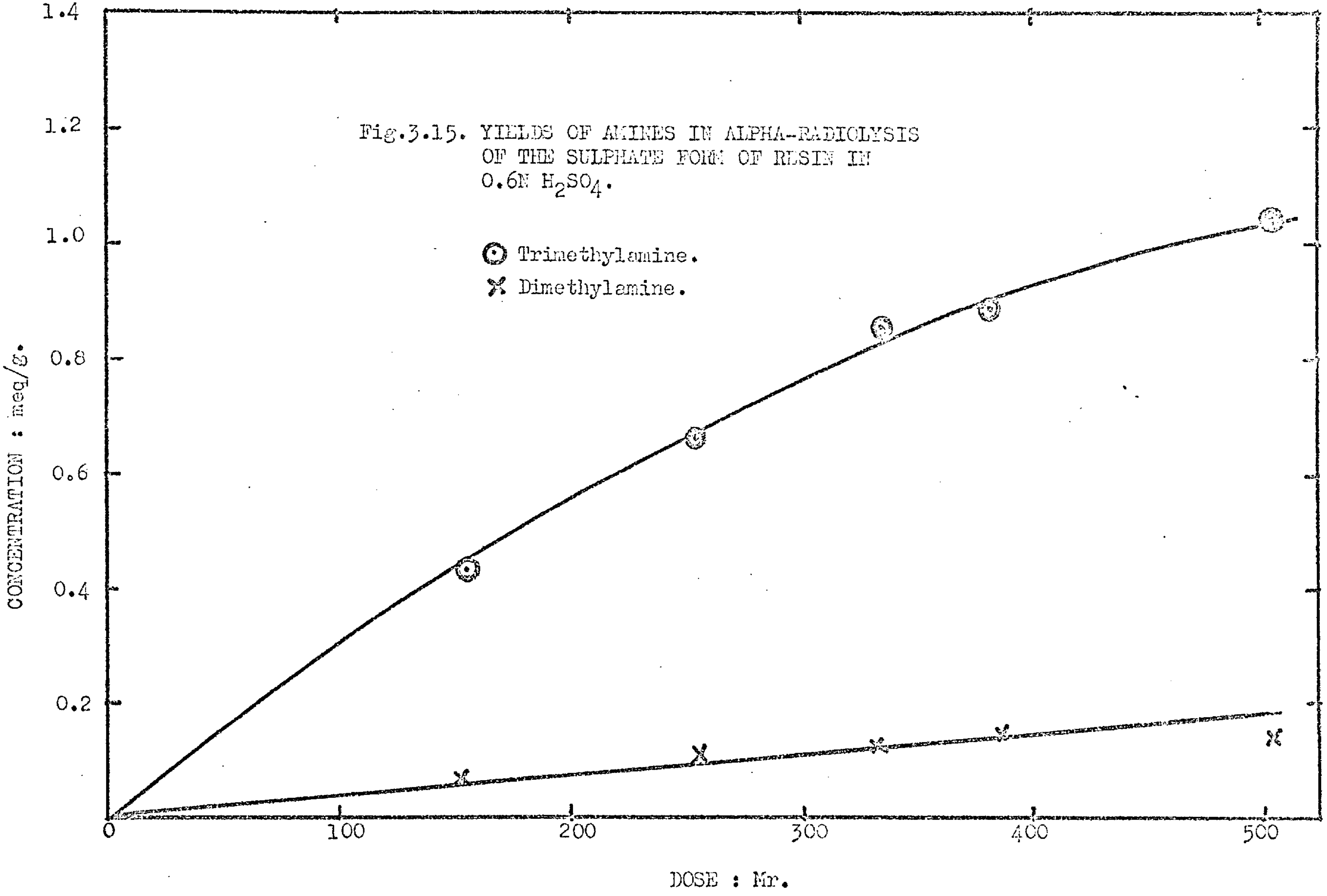


Fig.3.15. YIELDS OF AMINES IN ALPHA-RADIOLYSIS OF THE SULPHATE FORM OF RESIN IN 0.6N H_2SO_4.

It was mentioned above that the initial concentrations of the strong base functional groups in the chloride and the sulphate forms of resin are 4.5 and 2.90 respectively. The lower strong base and higher weak base capacities relative to those found in the chloride form of resin may be due to two factors.

(i) During drying at 105°C. overnight, the sulphate form of resin possibly lost functional groups. In fact, in the washings of the unirradiated sulphate form of resin 0.286 meq/g. of trimethylamine was found. The corresponding amount of trimethylamine from the chloride form of resin was about 0.02 meq/g. This indicates that the sulphate form of resin is more unstable towards heat than the chloride form. Klaschka(62) however finds that sulphate of the resin is more stable than the chloride form when heated at higher temperature, i.e. 150°C. in presence of water. This anomaly may be due to the presence or not of water.

(ii) The sulphate form of the resin may contain considerable amounts of $H\ SO_4^-$ ions and this can change the capacity to a considerable extent. This is because the meq. capacity of each form of the resin is measured in the same way but the capacity is related to the measured weight of the resin in the appropriate salt form. For example, when resin in the chloride form of capacity

4.5 meq/g. is converted to the $SO_4^=$ form, the capacity would theoretically be 4.2 meq/g., but if completely converted to HSO_4^- instead of the $SO_4^=$ form, the capacity would be 3.5 meq/g. (M.W. of resin unit in $SO_4^=$ form = 221, HSO_4^- form = 270. Similarly, in conversion of the chloride form of the resin to the phosphate form, the capacity would be almost equal in both cases, but if converted to $H_2PO_4^-$ or $HPO_4^=$, the capacity would be 3.5 or 4.2 meq/g. The actual capacity found in the phosphate form of resin is 3.50 meq/g. The sulphate and phosphate forms of resins thus appear to be largely in HSO_4^- and $H_2PO_4^-$ forms respectively. For convenience, however, this resin is referred to as being in sulphate or phosphate forms.

(b) γ-radiolyses of the chloride, sulphate and phosphate forms of the resins

The capacity changes due to γ-radiolyses of the three different salt forms of the resins have been tabulated (Table 3.9., 3.10. and 3.11.). Figs. 3.16., 3.17. and 3.18. show the strong base and the total capacity losses in all the three cases follow the same pattern. The rates of capacity losses decreased with increasing gamma radiation doses. Half the strong base capacity losses in the chloride, sulphate and phosphate forms occurred at 215, 165 and 200 Mr. respectively. The initial strong base capacities of the chloride and phosphate forms of resins used for γ-radiolysis are the same, i.e. 3.5 meq/g., but the sulphate form of resin has the initial strong base capacity of 2.9 meq/g. The lower half life for the sulphate form (165 Mr.) compared to the chloride and phosphate forms of resins (200 Mr.) is obviously due to the initial strong base capacity difference, for example, in the former case 1.45 meq/g. of strong base capacity change is brought about by 165 Mr. while in the latter cases, 1.75 meq/g. is brought about by 200 Mr. The G-decomposition of the total and strong base capacities and G-production of weak base capacities of the three salt forms of resins at the doses of 100 Mr. and 500 Mr. are shown in Table 3.12. From these results, it is clear that the three salt forms of resins, i.e. in the chloride, sulphate and phosphate forms undergo the same extent of decomposition per unit γ-dose. For example, the G-decomposition of the strong base capacities at the first 100 Mr. of γ-dose are 9.7, 9.2 and 9.2 for the chloride, sulphate and phosphate forms respectively, demonstrating that the stability of these resins towards γ-radiation is independent of the ionic form. The alpha radiation induced decomposition of the chloride, sulphate and nitrate forms of resins have also demonstrated the same conclusion, G-decomposition of the strong base capacity at the first 100 Mr. being 4.5, 4.1 and 4.1 for the chloride, sulphate and nitrate forms respectively. (Table 3.12.and 3.6.).

Table 3.9 : Gamma irradiation of chloride form of resin slurried in water : variation with dose of exchange capacities and yields of amines.

Dose Mr.	Measured capacities meq/g.		Capacity correction. meq/g.	Corrected capacities meq/g.		Chloride in leach solution meq/g.	$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	CH_3NH_2 meq/g.
	Weak base.	Strong base.		Weak base.	Strong base.				
Nil	0.59	3.40	0.23	0.36	3.63	Nil	Nil	Nil	Nil
45	0.64	2.91	0.20	0.44	3.11	0.40	0.40	0.01	0.002
145	0.80	1.99	0.26	0.54	2.25	1.24	1.09	0.07	0.006
220	0.80	1.72	0.20	0.60	1.92	1.49	1.27	0.12	0.007
387	1.11	0.67	0.29	0.82	0.96	2.20	1.72	0.19	0.010
500	1.12	0.56	0.27	0.84	0.83	2.22	1.85	0.31	0.012

Table 3.10: Gamma irradiation of sulphate form of resin slurried in water : variation with dose of exchange capacities, yields of amines, swelling weight and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction. meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	Swelling weights g.H_2O/g	% loss in resin weights.
	Weak base.	Strong base.		Weak base.	Strong base.				
Nil	0.76	2.60	0.30	0.46	2.90	Nil	Nil	0.81	Nil
100	0.82	1.63	0.32	0.50	1.95	0.78	0.064	-	-
150	0.95	1.18	0.42	0.53	1.60	1.03	0.082	0.83	9.0
204	0.89	0.86	0.33	0.55	1.19	1.31	0.102	0.83	29.0
326	1.04	0.29	0.41	0.63	0.69	1.65	0.120	0.69	34.7
492	0.79	0.17	0.10	0.69	0.27	2.05	0.148	0.52	30.5

Table 3.11 : Gamma irradiation of phosphate form of resin slurried in water : variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction.	Corrected capacities meq/g.		$(CH_3)_3N$	$(CH_3)_2NH$	Swelling weights	% loss in resin weights.
	Weak base.	Strong base.	meq/g.	Weak base.	Strong base.	meq/g.	meq/g.	$g.H_2O/g$	
Nil	0.24	3.29	0.27	0.03	3.50	Nil	Nil	0.80	Nil
93	0.37	2.40	0.25	0.12	2.65	0.70	0.019	1.10	15.0
187	0.65	1.59	0.25	0.41	1.84	1.20	0.069	1.09	24.5
255	0.64	1.26	0.30	0.34	1.56	1.52	0.082	1.04	30.0
465	0.80	0.42	0.37	0.43	0.79	1.95	0.130	0.71	37.0

Table 3.12. G-values for the decomposition of resins.

Type of Radiation	Form of resin	Dose Mr.	-G total capacity	-G strong base capacity.	+ G weak base capacity.	$+G(CH_3)_3N$
α-particle	Chloride	100	4.2	4.50	0.32	3.9
		500	3.2	4.50	1.16	2.9
α-particle	Sulphate	100	3.40	4.10	0.55	2.9
		500	2.31	2.9	0.55	2.0
γ-ray	Chloride	100	8.7	9.7	0.93	7.5
		500	4.41	5.8	0.93	3.6
γ-ray	Sulphate	100	8.3	9.2	0.67	7.5
		500	4.61	6.0	0.67	3.9
γ-ray	Phosphate	100	7.4	9.2	1.6	7.5
		500	5.61	5.4	0.84	3.9

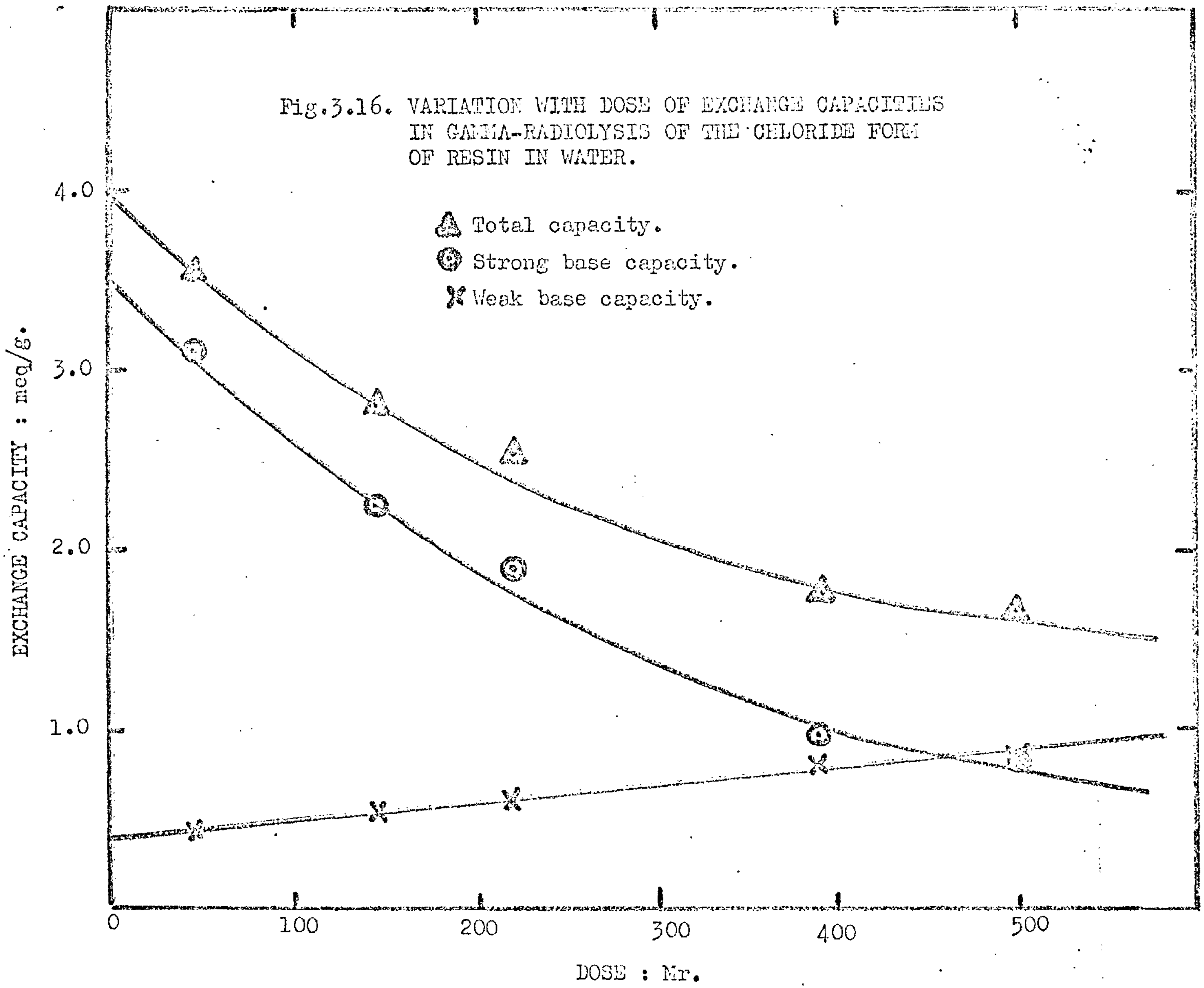


Fig.3.16. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN GAMMA-RADIOLYSIS OF THE CHLORIDE FORM OF RESIN IN WATER.

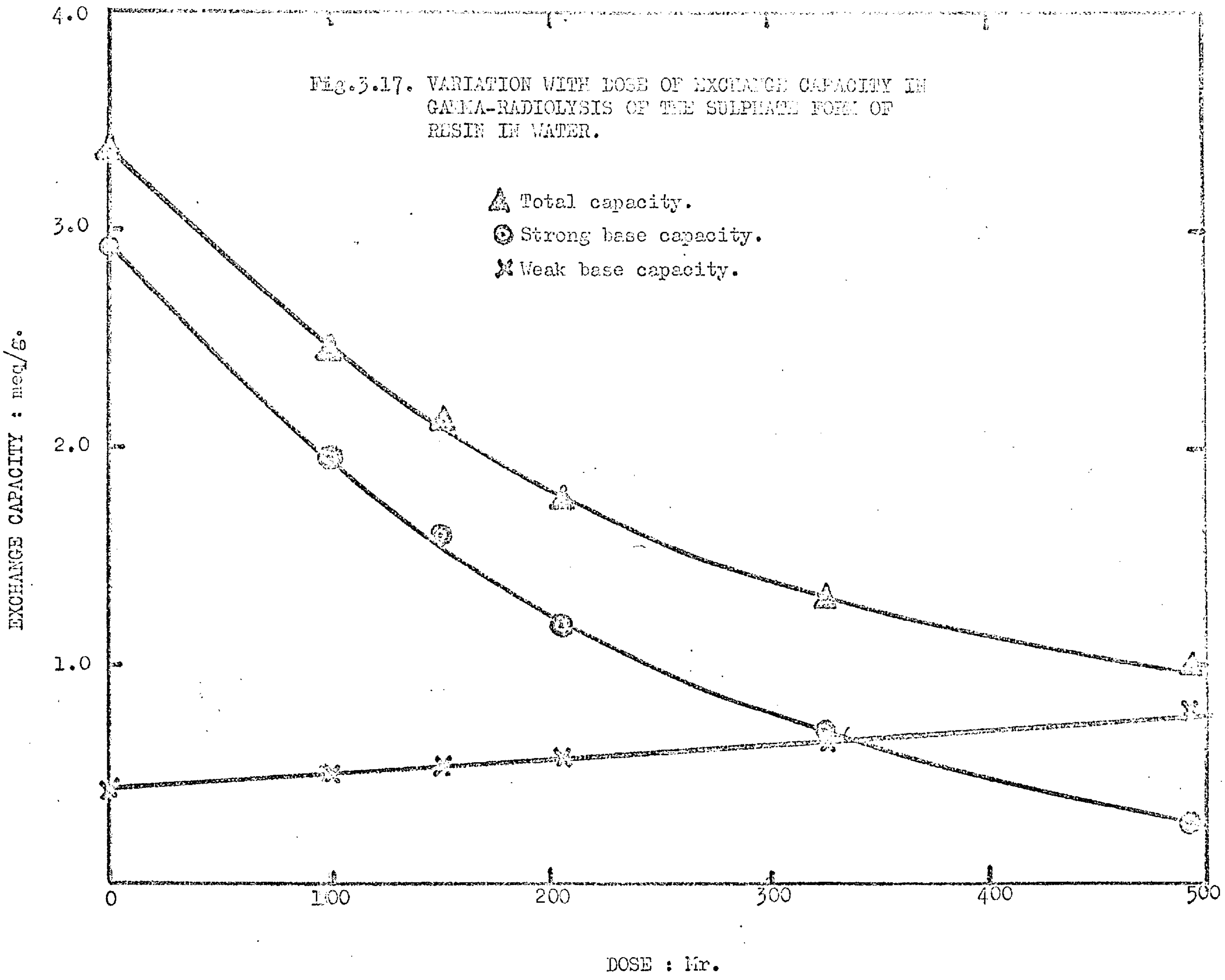


Fig.3.17. VARIATION WITH DOSE OF EXCHANGE CAPACITY IN GAMMA-RADIOLYSIS OF THE SULPHATE FORM OF RESIN IN WATER.

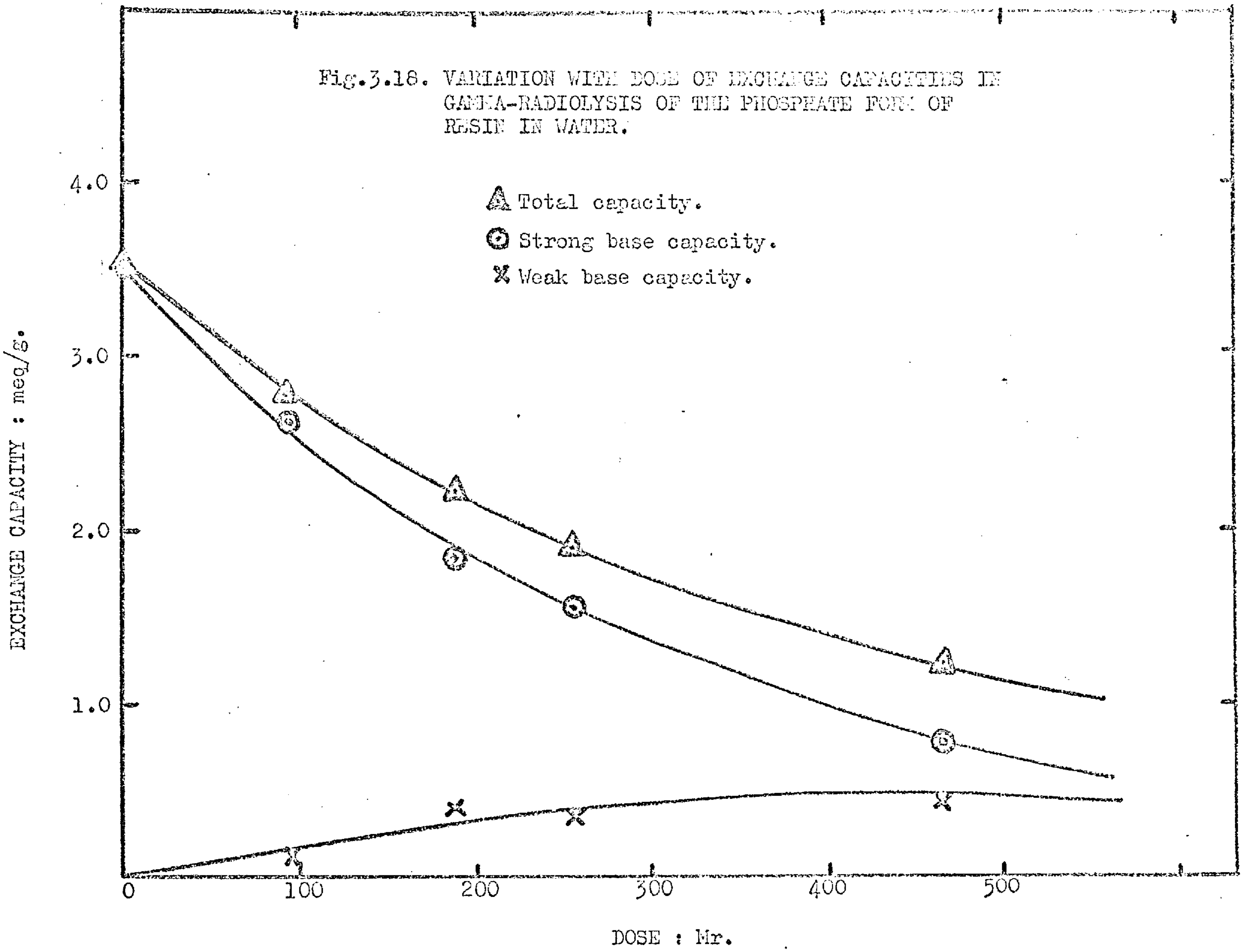


Fig.3.18. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN GAMMA-RADIOLYSIS OF THE PHOSPHATE FORM OF RESIN IN WATER.

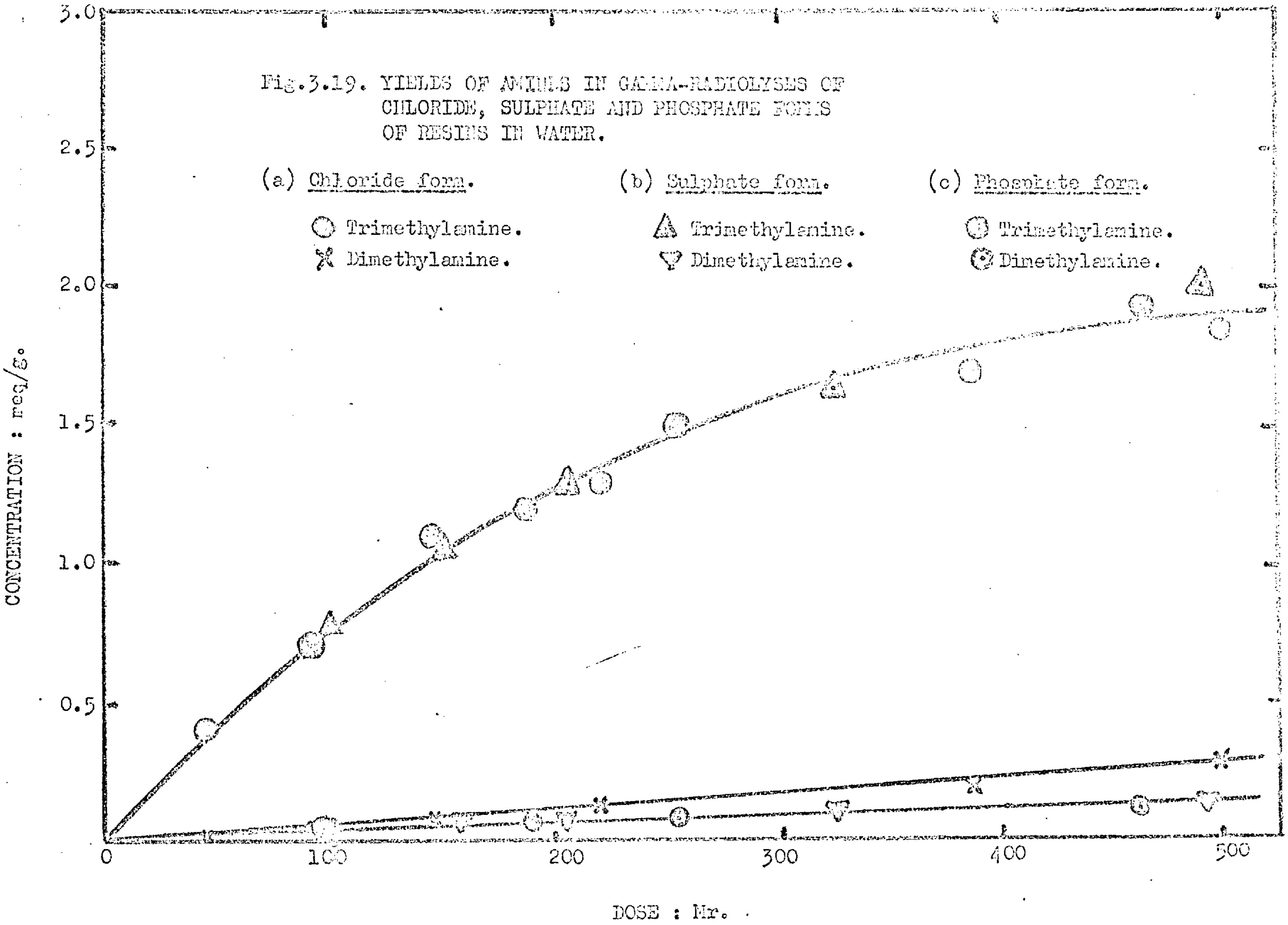


Fig.3.19. YIELDS OF AMINES IN GAMMA-RADIOLYSES OF CHLORIDE, SULPHATE AND PHOSPHATE FORMS OF RESINS IN WATER.

It may however be mentioned that the nitrate form of resin was found to be unusually stable towards γ-radiation(16). The causes of the unusual stability of this exceptional case are investigated and discussed in Chapter 4.

A study of radiation induced decomposition of the salt forms of resins has also shown that the resins are twice as stable towards alpha radiation than gamma radiations, G-strong base capacity decomposition being 4.1-4.5 and 9.2-9.7 respectively.

Basic Products

(a) Alpha radiolysis of the chloride and sulphate forms of resins.

The yields of basic products due to alpha radiolysis of the two salt forms are shown in Tables 3.7. and 3.8., and Figs. 3.13. and 3.15. With increasing alpha dose, the trimethylamine yield from the chloride form of resin in $\sim 10^{-3}$N HCl increases more rapidly than the sulphate form of resin in 0.6N H_2SO_4. Figs.3.13. and 3.15. show that at 500 Mr. the trimethylamine yield from the chloride form of resin is 1.5 meq/g., while from the sulphate the yield is 1.0 meq/g. This may be attributed to the lower concentration of the functional group present in the sulphate form at higher doses. For example, at 500 Mr. the strong base capacities retained in the chloride and sulphate forms are 2.25 and 1.45 meq/g. respectively and at this stage in the latter case the energy absorbed becomes less effective in splitting off functional groups. From the comparison of $G(CH_3)_3N$ for both the salt forms, (Table 3.12.) it can be seen that the chloride form having a higher concentration of functional groups than the sulphate form undergoes more rapid decomposition at both the doses, i.e. 100 Mr. and 500 Mr. The dimethylamine yield in the chloride form of resin is observed to be higher than that in the sulphate form, the yields at 500 Mr. being 0.23 and 0.14 meq/g. respectively.

(b) γ-radiolysis chloride, sulphate and phosphate forms of resins.

In the γ-radiolysis of the chloride, sulphate and phosphate forms of resins in aqueous media, the trimethylamine is found to be the major product and the yield increases with increasing γ-dose, but at higher doses, the rate of production of the amine is reduced. This has been observed in all the three salt forms. Fig.3.19. shows that the secondary decomposition of the trimethylamine to dimethylamine cannot alone explain the decreased yield of trimethylamine but it is rather a consequence of the lower concentration of the functional groups remaining in the resin at higher doses than at the initial. It is interesting to note that yield is almost exactly the same in all the three cases (Fig.3.19.) and(Table 3.12) and clearly demonstrates that the three salt forms are of similar radiation stability.

The dimethylamine is found to increase linearly with increasing dose, in all the three forms of resins. The yield from the chloride form of resin is slightly higher than the sulphate and phosphate forms. It is also noted that the sulphate form of resin had initially a higher weak base capacity (0.45 meq/g.) and yet the dimethylamine produced in its radiolysis is less than both the phosphate and chloride resins (Fig. 3.19.). This again shows that dimethylamine is not only produced by the decomposition of weak base groups but also by the secondary radiolytic decomposition of the trimethylamine. The dimethylamine yield is very low compared to that of trimethylamine (the ratio of trimethylamine to dimethylamine in phosphate and sulphate is 20:1 and in chloride form 10:1). Thus at least 90-95% of the total capacity loss which is the sum effect due to the removal of $-N(CH_3)_3$ and $-N(CH_3)_2$ from the resin, can be accounted for by trimethylamine yield only.

Swelling weights

The swelling weights due to the alpha radiolysis of the resins increased with increasing radiation dose (Fig.3.22.). The rate of increase in both the chloride and sulphate forms is the same up to about 175 Mr. Above this dose, the swelling weight of the chloride form resin continues to increase while it starts decreasing in the sulphate form.

The swelling weight due to γ-radiolysis of phosphate form also increased with increasing radiation dose up to about 150 Mr. Above this dose it decreased with further increases in dose. The γ-radiolysis of the sulphate form however showed that the swelling weight remained unchanged up to about 250 Mr. and, above this dose, it decreased.

The increase and decrease of swelling weights are known to **result from** decrosslinking and crosslinking in the resin polymer matrix. Creed(17) by a diffusion study on the irradiated resin has shown that the swelling weight decrease is associated with an increase in crosslinking in the resin polymer.

In general, it was observed in this work that alpha radiation causes decrosslinking of the resin while in γ-radiation, crosslinking is more prominent. This is evidenced from alpha radiolysis of the nitrate (Fig.3.11.), chloride and sulphate forms (Fig.3.22.) and γ-radiolysis of sulphate and phosphate forms (Fig.3.22.). The rupture of C-N bonds in the resins results in polymeric radicals which can react with each other to produce crosslinking in the resin. Kiseleva et al(49) consider that decrosslinking in a resin occurs through reactions of radiolytic H., .OH , NO_2 etc. with polymeric radicals, resulting in enhanced polarity and hence increased swelling weights.

It is thus clear that the swelling weight changes is an extremely complex function of the type of radiation, media, ionic groups present, extent of the functional groups present etc.

Weight losses

The weight losses have been observed to increase with the increase of both α and γ-radiation doses. Figs. 3.20.1 to 3.21.2. show the losses in weights expected from the removal of $N(CH_3)_3X^-$ and CH_3 due to radiolysis and the experimental values found (X^- represents an exchangeable anion).

It can be seen that for a given dose, γ-radiation caused a greater loss in weight than α-radiation, this difference being brought about by the fact that G (-functional groups) was highest in the case of γ-irradiation.

In all cases, the weight losses found experimentally were higher than those calculated (Figs.3.20. 1-3.21.2). This difference may be attributed to the dissolution of the polymer network. The maximum dissolution of the polymer was found to be 5.0% of the total weight, in the γ-dose range of 200-300 Mr. Above 300 Mr. γ-dose, the rate of weight loss has been considerably reduced.

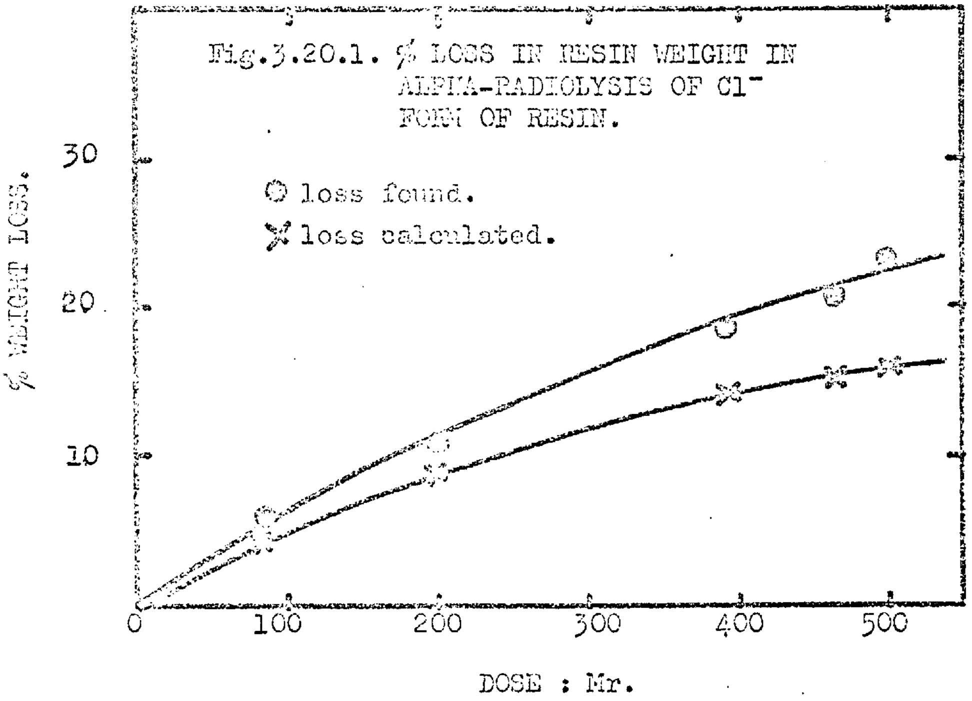


Fig.3.20.1. % LOSS IN RESIN WEIGHT IN ALPHA-RADIOLYSIS OF Cl^- FORM OF RESIN.

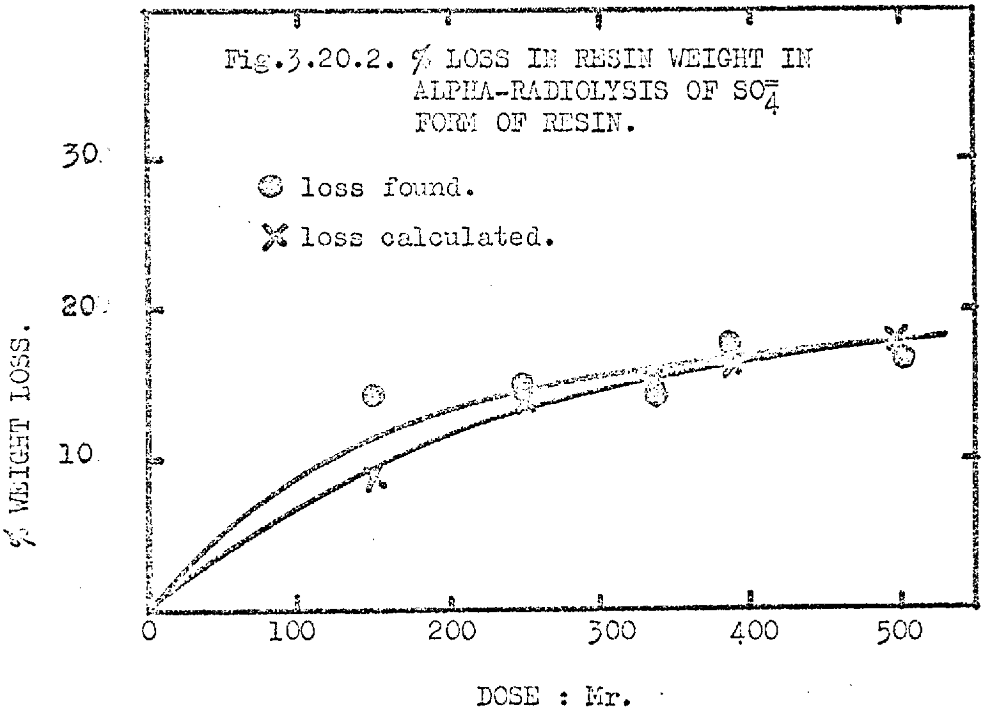


Fig.3.20.2. % LOSS IN RESIN WEIGHT IN ALPHA-RADIOLYSIS OF $SO_4^=$ FORM OF RESIN.

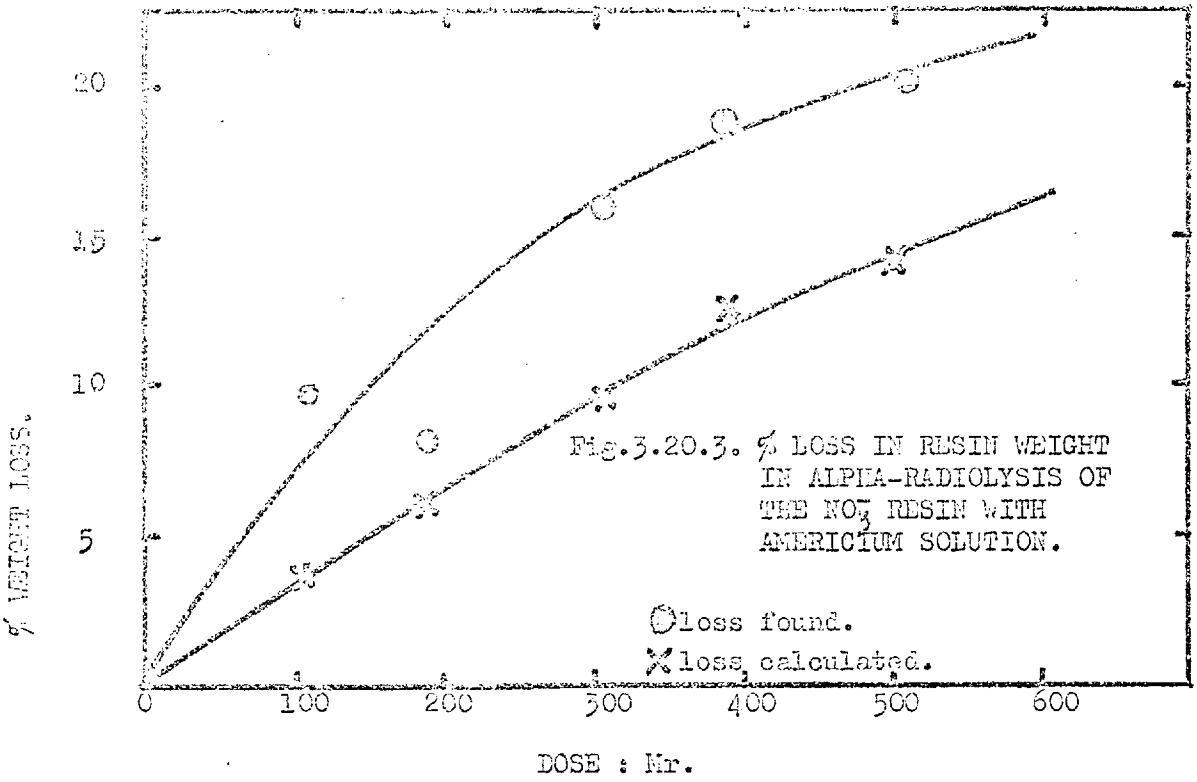


Fig.3.20.3. % LOSS IN RESIN WEIGHT IN ALPHA-RADIOLYSIS OF THE NO_3^- RESIN WITH AMERICIUM SOLUTION.

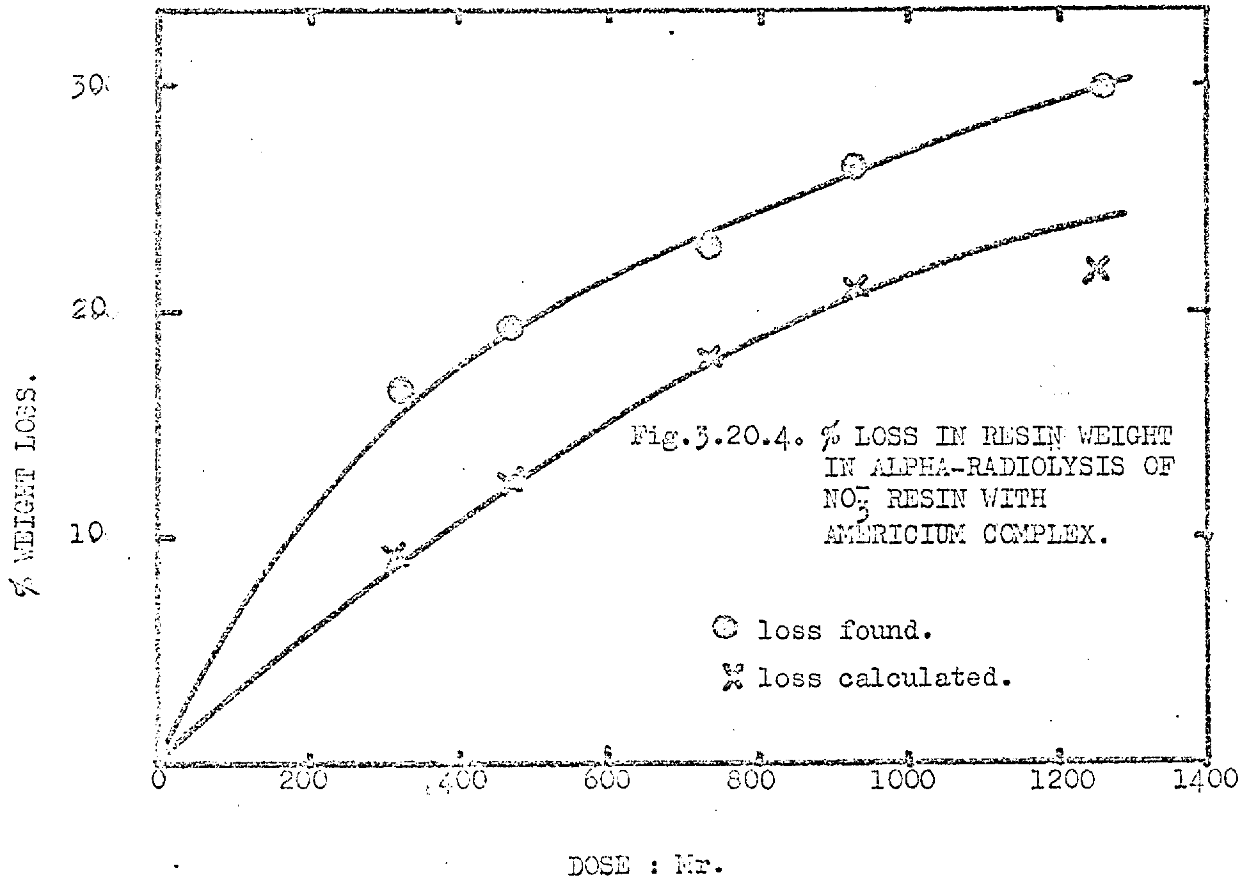


Fig.3.20.4. % LOSS IN RESIN WEIGHT IN ALPHA-RADIOLYSIS OF NO_3^- RESIN WITH AMERICIUM COMPLEX.

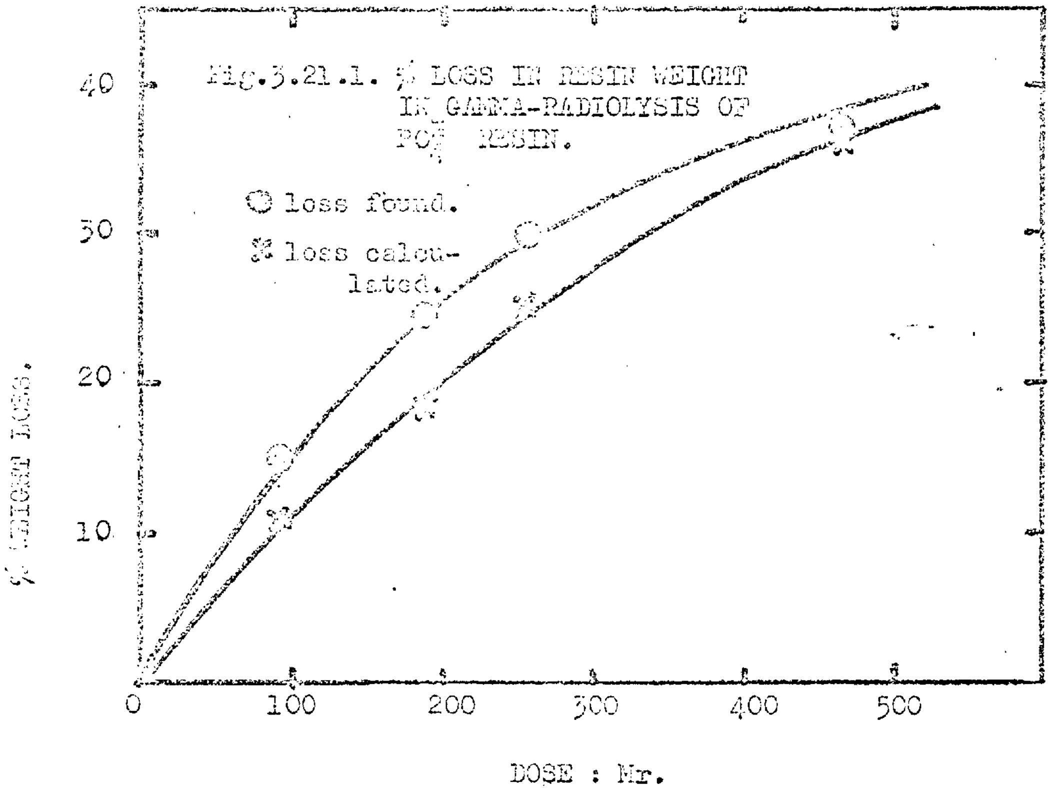


Fig.3.21.1. % LOSS IN RESIN WEIGHT IN GAMMA-RADIOLYSIS OF $PO_4^{\equiv}$ RESIN.

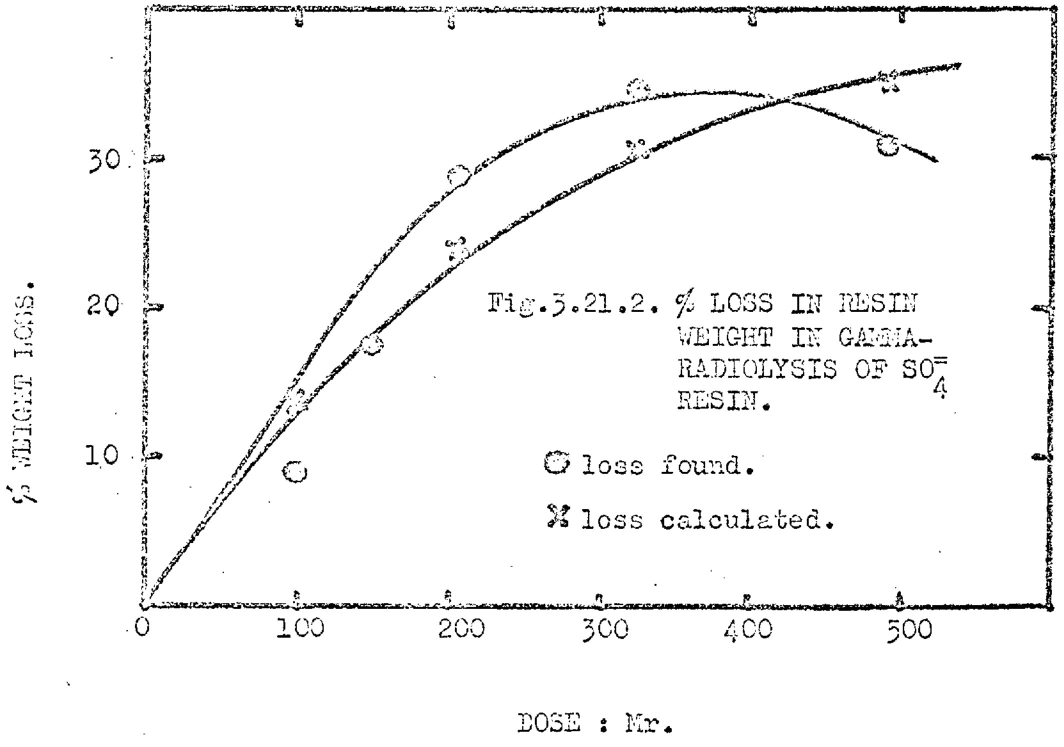


Fig.3.21.2. % LOSS IN RESIN WEIGHT IN GAMMA-RADIOLYSIS OF $SO_4^{=}$ RESIN.

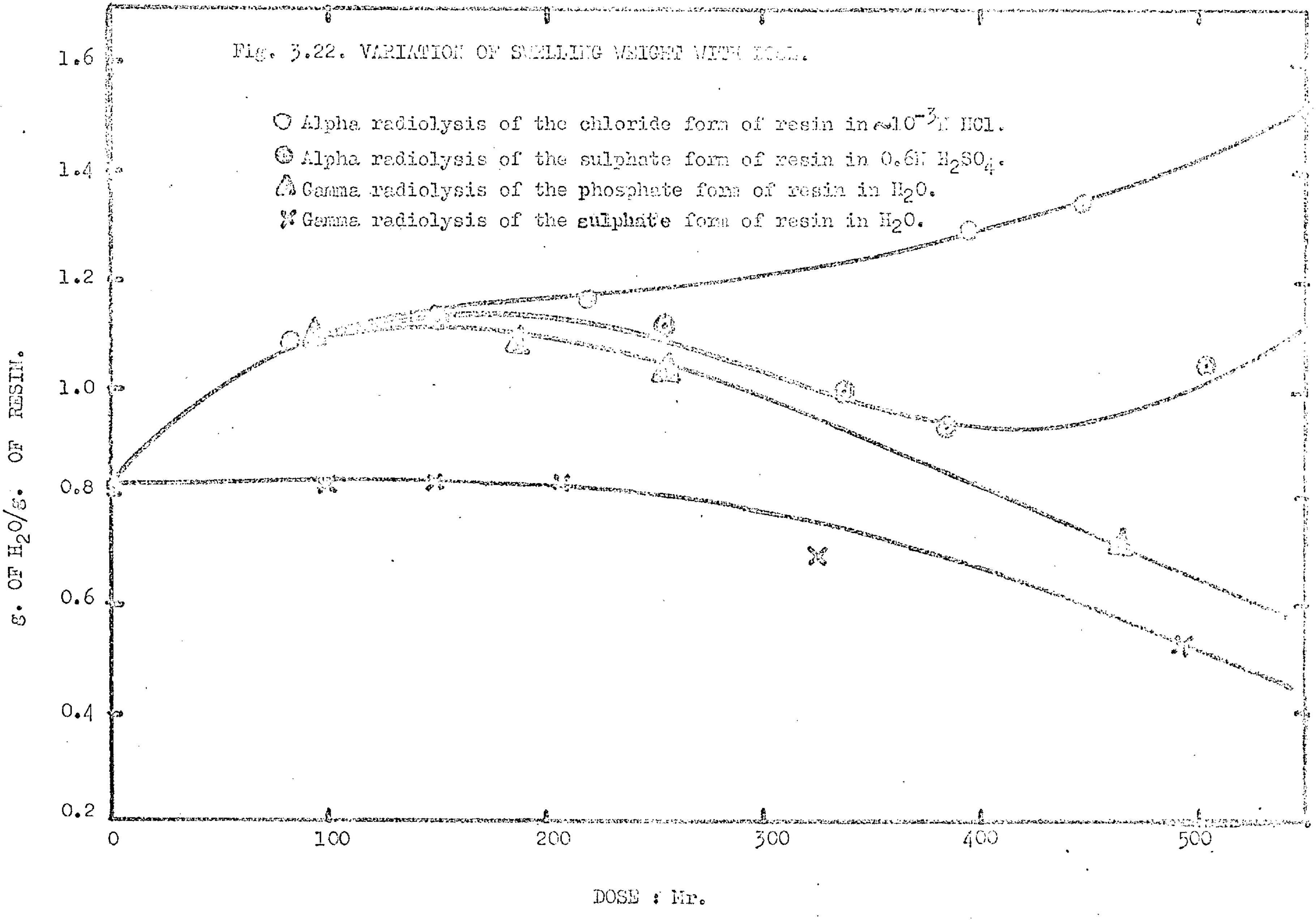


Fig. 3.22. VARIATION OF SWELLING WEIGHT WITH DOSE.

This was possibly due to reduced rate of deamination in this dose range.

In α-particle radiolysis of Cl^- and NO_3^- resins, the rate of deamination has not been reduced to a great extent even at 500 Mr. and the weight losses in α-radiolysis of the resins also followed this behaviour, the weight losses continually increasing with increasing α-dose. The weight losses in α-radiolysis of nitrate resin were found to be much higher than the calculated values. The dissolution of polymers in this case was presumably enhanced by reactions involving the radiolytic products of HNO_3, i.e. NO_2, NO_2^-, O_2 etc.

In this section, the α and γ-radiation-induced decompositions of anion exchange resins and the stability dependence of anionic forms have been discussed. All the γ-radiolyses have been carried out by slurrying the resin in H_2O. α-particle radiolyses have been done by slurrying the resin in americium solution in dilute acids. It was suspected, however, that hydrogen ion concentration might influence decomposition.

3.3.3. Effect of hydrogen ion concentration on the radiation stability of an anion exchange resin.

Most of the data on the radiation-induced decomposition of anion exchange resins relates to irradiations in neutral aqueous media. The irradiation of anion exchange resins has however been studied in 7M HNO_3 both by Ahrens(24) and Natarajan(16) and the latter observed considerable dissolution of the resin at high doses under these conditions.

A more general study of the effect of hydrogen ion on the alpha and gamma irradiation of anion exchange resin was considered important.

The alpha-particle irradiations of nitrate and chloride forms of resin brought about by slurrying the resins in americium solution of low acidity ($\sim 10^{-3}$N) have been reported in sections 3.3.1. and 3.3.2. In these experiments the acidity was kept to its minimum so that the α-particle irradiation results could be compared with those of γ-irradiations in neutral aqueous medium.

In the experiments described in this section, acid concentrations of 0.5-0.7N were utilised for both α- and γ-irradiations. It was believed that this concentration of acid would be sufficiently high to observe the effects due to changing H^+ without introducing possible complications from having the resin in contact with very strong acid. The irradiations were carried out on Cl^-, NO_3^- and $SO_4^=$ salt forms of the resin slurried with 0.5-0.7N solutions of the appropriate acids.

Capacity changes:

(a) Alpha radiolysis of chloride and nitrate forms of resin.

The results of the α-particle irradiations of Cl^- form of the resin in presence of 0.7N HCl are shown in Table 3.13. and Fig.3.23. and can be compared with those obtained in 10^{-3}N HCl (Fig.3.12.). It is apparent that less decomposition occurs at the higher acid concentration. 50% loss of strong base capacity is brought about at 675 Mr. compared with 465 Mr. required in $\sim 10^{-3}$N HCl. In the more acid solution, the % of strong base converted to weak base is 10% at 675 Mr., compared with 13.5% observed for the weaker acid at 465 Mr. The capacity changes due to alpha radiolysis of the nitrate form of resin in 0.5N HNO_3 have been shown in Table 3.14. Fig.3.25. shows that 50% of the strong base capacity is lost at 550 Mr. In section 3.3.1., Fig.3.9., it was shown that the same resin in $\sim 10^{-3}$N HNO_3 lost only 45% of its strong base capacity even at the higher dose of 600 Mr. This shows that the decomposition of the nitrate resin by alpha radiolysis is slightly enhanced by the increase in HNO_3 concentration. Since it was observed that hydrogen ion protected

Table 3.13 : Alpha particle irradiation of chloride form resin slurried in 0.7N HCl : variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction. meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	CH_3NH_2 meq/g.	NH_3 meq/g.	Total volatile base. meq/g.	Swelling weights g.H_2O/g.	%loss in resin weights.
	Weak base.	Strong base.		Weak base.	Strong base.							
Nil	0.52	4.10	0.45	0.07	4.55	Nil	Nil	Nil	Nil	Nil	0.82	Nil
88	0.65	3.38	0.56	0.09	3.94	0.27	0.05	0.023	Nil	0.41	1.15	5.0
184	0.78	3.32	0.50	0.28	3.82	0.46	0.10	0.027	Nil	0.59	1.16	6.0
315	0.79	2.85	0.49	0.30	3.33	0.65	0.15	0.044	Nil	0.77	1.15	10.5
410	0.82	2.67	0.47	0.35	3.14	0.77	0.18	0.052	Nil	1.35	1.11	10.0
505	0.81	2.38	0.41	0.40	2.79	0.80	0.20	0.045	Nil	0.98	1.17	17.5

Dose rate 10 Mr/day.

Chloride resin slurried with $AmCl_3$ solution in 0.7N HCl.

Table 3.14: Alpha particle irradiation of nitrate form of resin slurried in 0.5N HNO_3 : variation of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction. meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	Swelling weights g.H_2O/g	% loss in resin weights.
	Weak base.	Strong base.		Weak base.	Strong base.				
Nil	0.26	3.79	0.21	0.05	4.00	Nil	Nil	0.82	Nil
91	0.48	3.26	0.26	0.22	3.53	0.24	0.077	1.10	17.5
200	0.74	2.80	0.29	0.45	3.09	0.44	0.128	1.27	20.0
360	1.54	2.26	0.52	1.02	2.78	0.78	0.115	1.31	21.0
428	1.28	1.54	0.54	0.74	2.08	0.82	0.136	1.41	26.5
510	1.75	1.09	1.10	0.64	2.19	0.95	0.155	1.37	26.0

Dose rate of 10 Mr/day.

Nitrate resin slurried with $Am(NO_3)_3$ solution in 0.5N HNO_3.

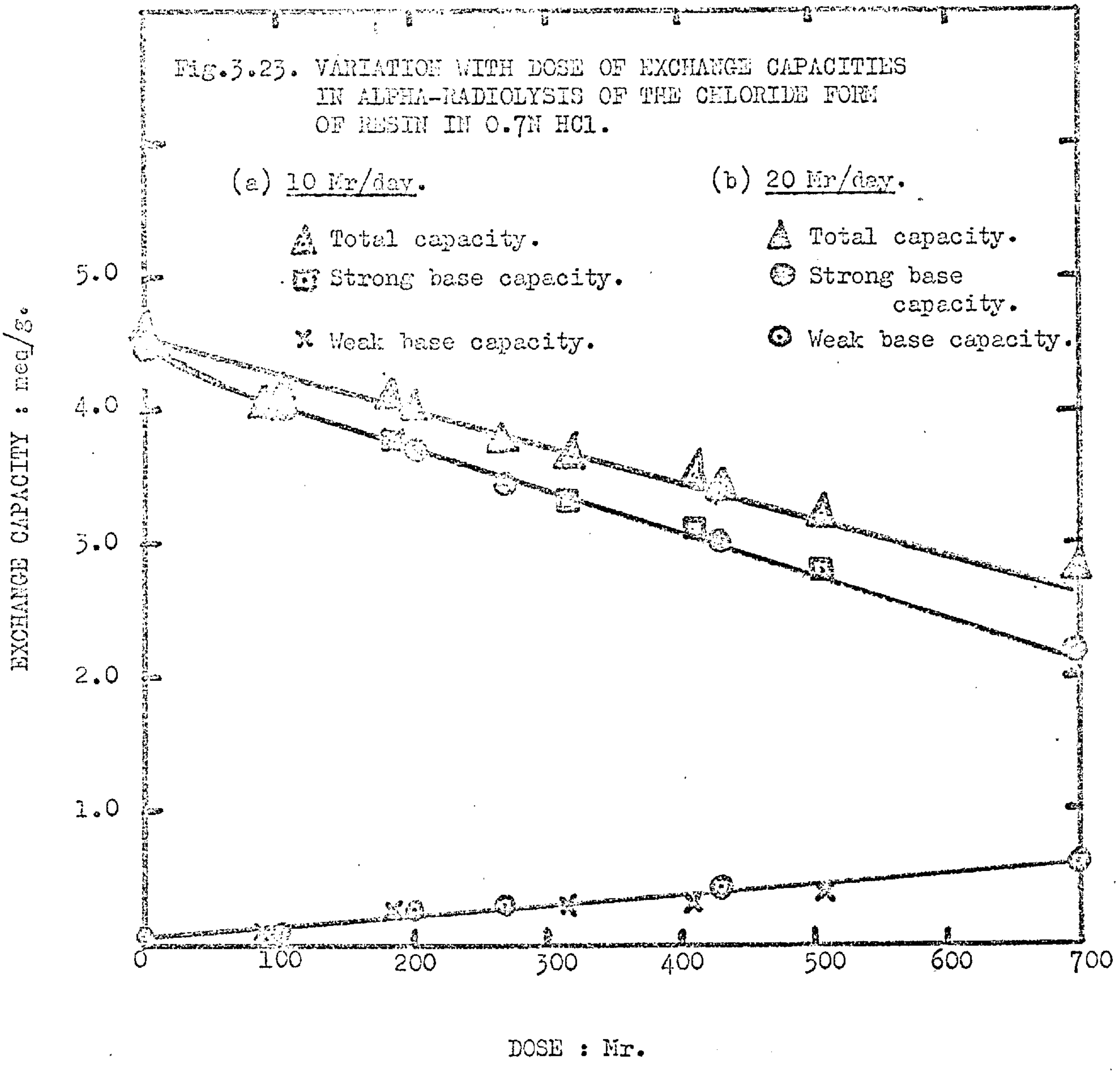


Fig.3.23. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN ALPHA-RADIOLYSIS OF THE CHLORIDE FORM OF RESIN IN 0.7N HCl.

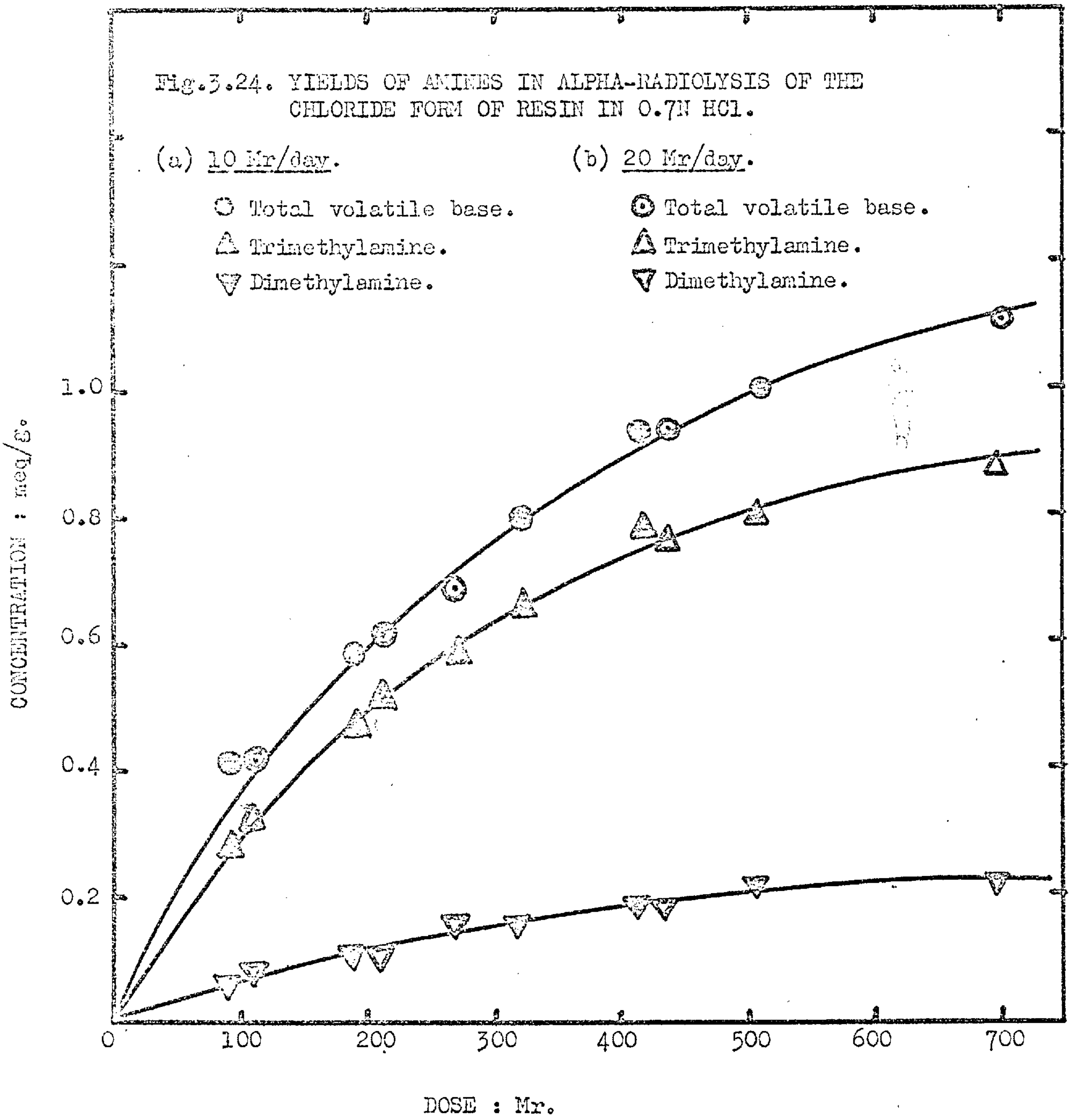


Fig.3.24. YIELDS OF AMINES IN ALPHA-RADIOLYSIS OF THE CHLORIDE FORM OF RESIN IN 0.7N HCl.

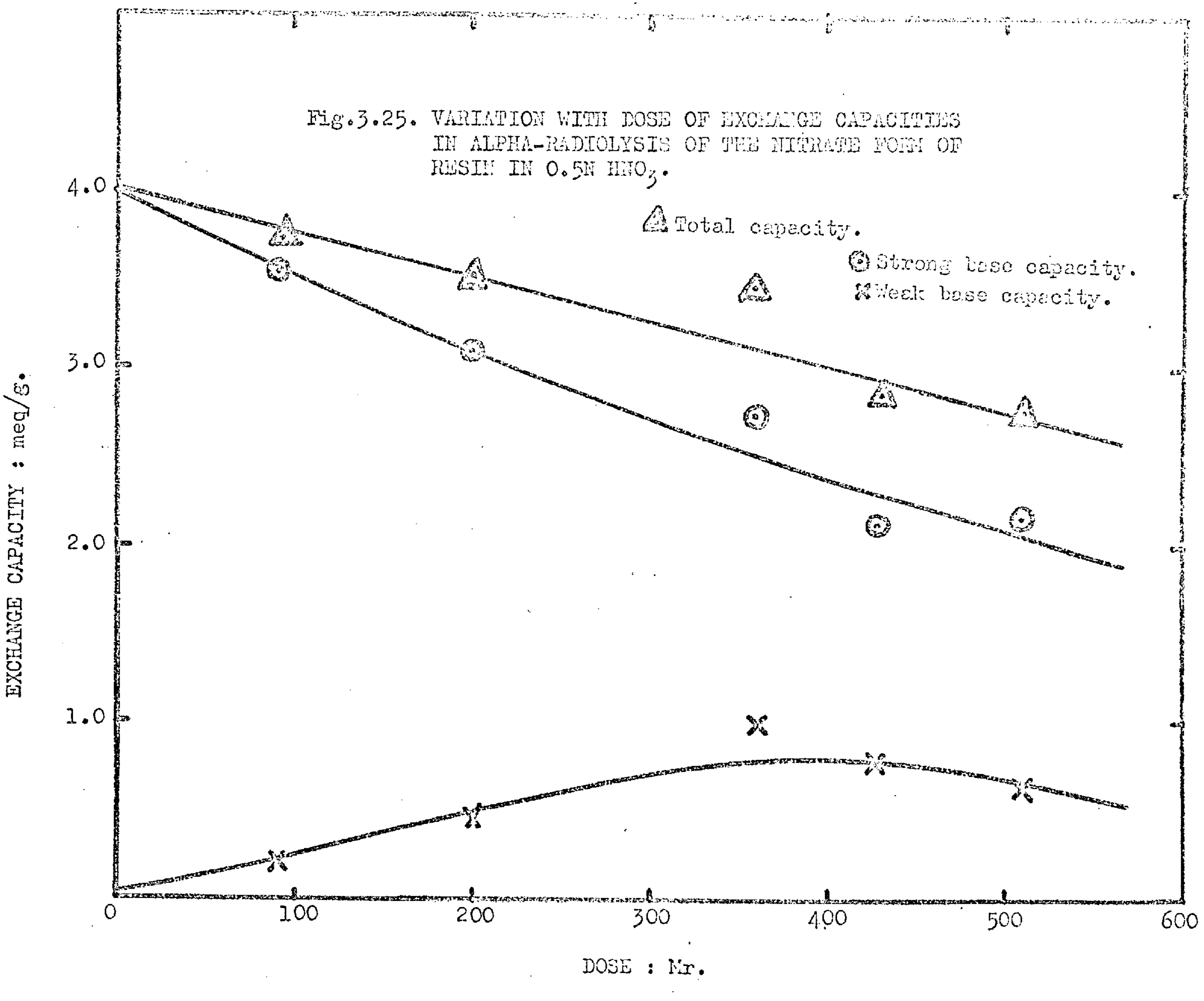


Fig.3.25. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN ALPHA-RADIOLYSIS OF THE NITRATE FORM OF RESIN IN 0.5N HNO_3.

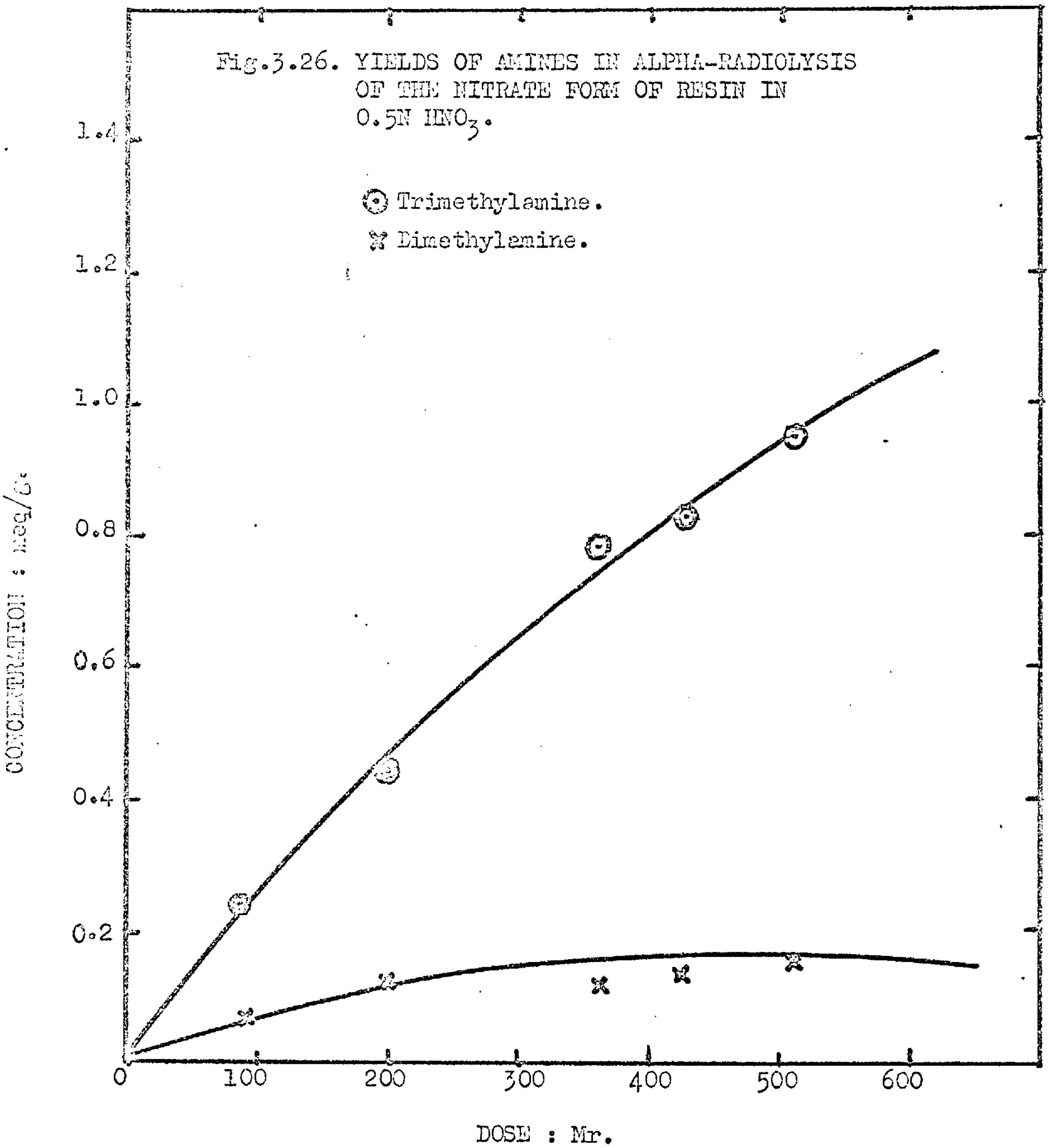


Fig.3.26. YIELDS OF AMINES IN ALPHA-RADIOLYSIS OF THE NITRATE FORM OF RESIN IN 0.5N HNO_3.

the chloride form of resin to some extent from radiolytic decomposition, the enchanced decomposition of the nitrate form of resin in presence of increased HNO_3 concentration is possibly due to secondary reactions involved with the radiolytic products of the HNO_3. The difference though small is also demonstrated by the G-values for loss of strong base capacities and growth of weak base capacities (Tables 3.17. and 3.6.). From the higher G-value for weak base production in the presence of 0.5N HNO_3 (GWB = 1.6 at 100 Mr.) compared with that in presence of 10^{-3}N HNO_3 (GWB = 1.1 at 100 Mr.), it may also be concluded that the radiolytic products of HNO_3 bring about scission of $N-CH_3$ bonds, thus producing increased weak base capacity in the resin.

(b) γ-radiolysis of the chloride and sulphate forms of resins.

The capacity changes due to γ-radiolysis of the chloride and sulphate forms of resins in 0.7N acids are given in Tables 3.15. and 3.16. and Figs.3.27. and 3.29. The chloride form loses 50% of the strong base capacity at 262 Mr. In the previous section, it was shown that the same resin lost 50% of its strong base capacity at 215 Mr., when irradiated in aqueous slurry. The sulphate form of resin in 0.7N H_2SO_4 loses 50% strong base capacity at 187 Mr. In aqueous slurry, this resin was found to lose 50% of the strong base capacity at 165 Mr.

Both these resins show that the presence of hydrogen ions results in a lower rate of decomposition by γ-ray. Table 3.17. shows the G-values for decomposition of total and strong base capacities and the production of weak base capacities, and demonstrates effects of hydrogen ion in reducing G-values (cf. Table 3.12.).

Basic Products

(a) α-radiolyses of the chloride and nitrate forms of resins.

The yields of the total volatile base, trimethylamine and dimethylamine in the alpha radiolysis of the chloride in presence of 0.7N HCl increase with increasing radiation dose, but at higher doses the rates of the production of amines are reduced to a small extent (Fig.3.24.). The yields of trimethylamine and dimethylamine due to alpha radiolysis of the nitrate form of resin in 0.5N HNO_3 increases in a similar manner as in thechloride form of resin. A relatively greater yield of amine is found in the radiolysis of the chloride form of resin, for example at 100 Mr. (Table 3.17.) G-values of trimethylamine in chloride and nitrate forms are 2.9 and 2.5 respectively. At the same dose, the G-total volatile base is also higher in the former than the latter, the values being 3.7 and 2.9 respectively. This lower yield of the amines for the nitrate form is expected since

Table 3.15: Gamma irradiation of chloride form of resin slurried in 0.7NHCl : variation of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction. meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	Swelling weights.	% loss in resin weights.
	Weak base.	Strong base.		Weak base.	Strong base.				
0	0.59	3.30	0.25	0.34	3.55	Nil	Nil	0.82	Nil
95	0.78	2.48	0.27	0.51	2.75	0.70	0.045	0.81	11.5
205	0.83	1.74	0.23	0.60	1.97	1.18	0.092	0.79	27.0
280	0.87	1.49	0.27	0.60	1.76	1.42	0.149	0.76	24.0
483	0.96	0.87	0.22	0.74	1.09	1.97	0.180	0.60	30.0

Table 3.16 Gamma irradiation of sulphate form of resin slurried in 0.6 NH$_2$SO$_4$: variation of exchange capacities, yields of amines, swelling weights and loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction. meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	Swelling weights g.H_2O/g.	% loss in resin weights.
	Weak base.	Strong base.		Weak base.	Strong base.				
Nil	0.76	2.60	0.30	0.46	2.90	Nil	Nil	0.82	Nil
67	0.68	2.04	0.28	0.40	2.32	0.45	0.04	0.82	12.0
165	0.88	1.36	0.25	0.63	1.61	0.89	0.09	1.01	20.0
272	0.93	0.91	0.21	0.72	1.11	1.29	0.12	0.92	25.5
380	1.03	0.49	0.24	0.79	0.73	1.49	0.20	0.67	25.0

Table 3.17. G -values **for** decomposition of resins in presence of acids.

Form of resin	Radiation	Dose	-G total capacity.	-G Strong base capacity.	+G Weak base capacity.	$G(CH_3)_3N$
Chloride in 0.7N HCl	Alpha-particle	100	2.7	4.3	0.70	2.9
		500	2.7	3.3	0.70	1.6
Nitrate in 0.5N HNO_3	Alpha-particle	100	3.6	5.1	2.0	2.5
		500	2.7	3.7	1.3	1.7
Chloride in 0.7N HCl	γ-ray	100	6.5	7.9	1.8	5.7
		500	4.1	4.8	0.82	3.9
Sulphate in 0.6N H_2SO_4	γ-ray	100	7.3	8.5	1.20	5.8
		500	3.9	4.6	0.68	3.2

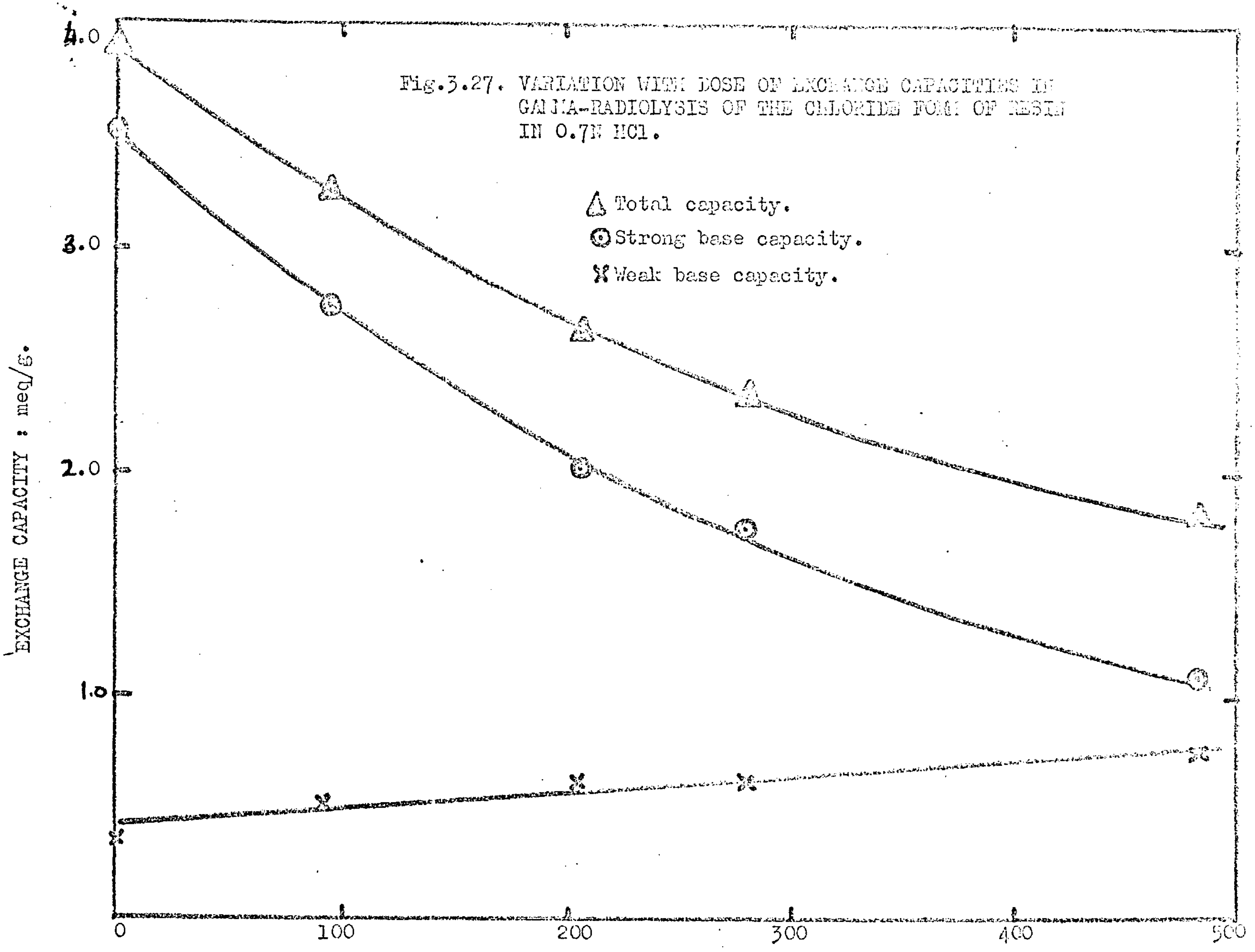


Fig.3.27. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN GAMMA-RADIOLYSIS OF THE CHLORIDE FORM OF RESIN IN 0.7N HCl.

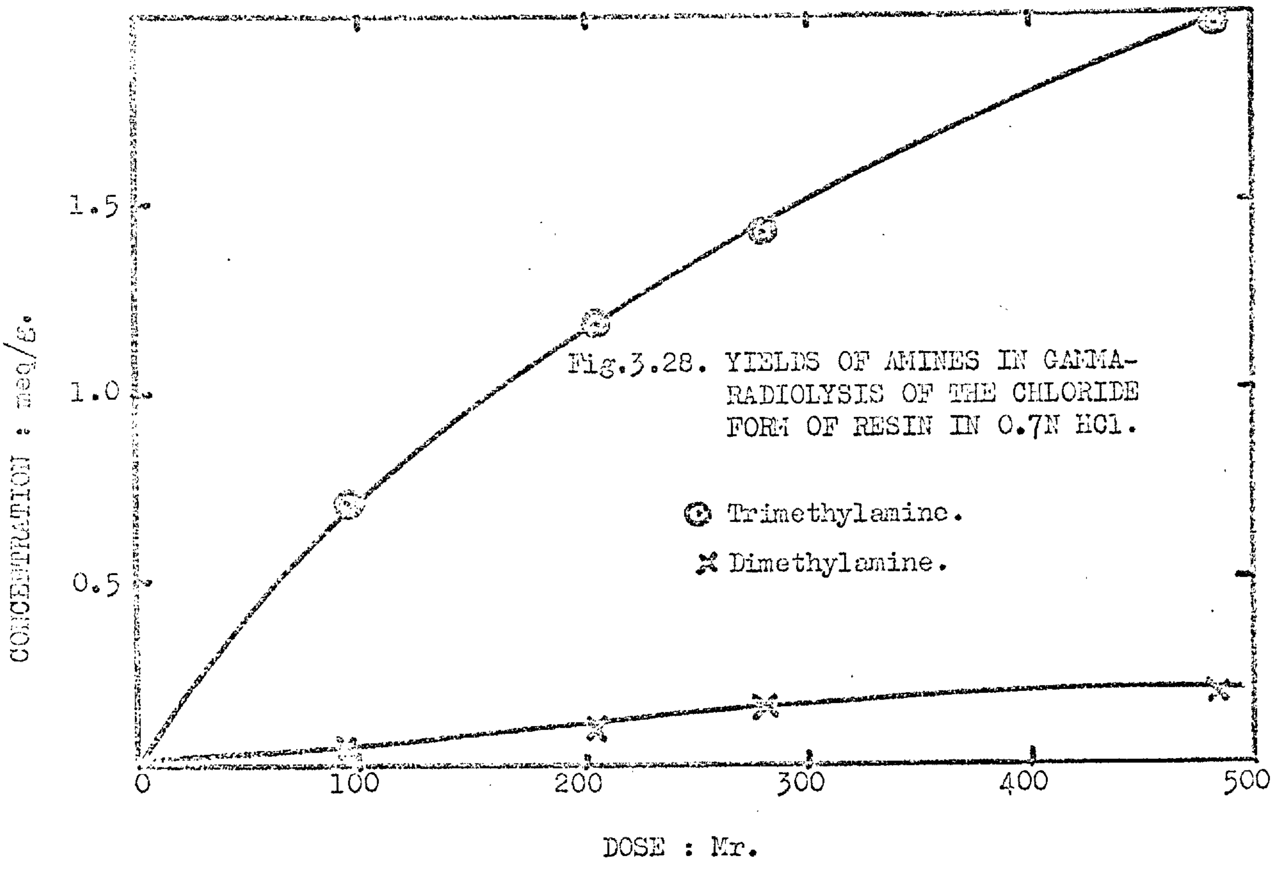


Fig.3.28. YIELDS OF AMINES IN GAMMA-RADIOLYSIS OF THE CHLORIDE FORM OF RESIN IN 0.7N HCl.

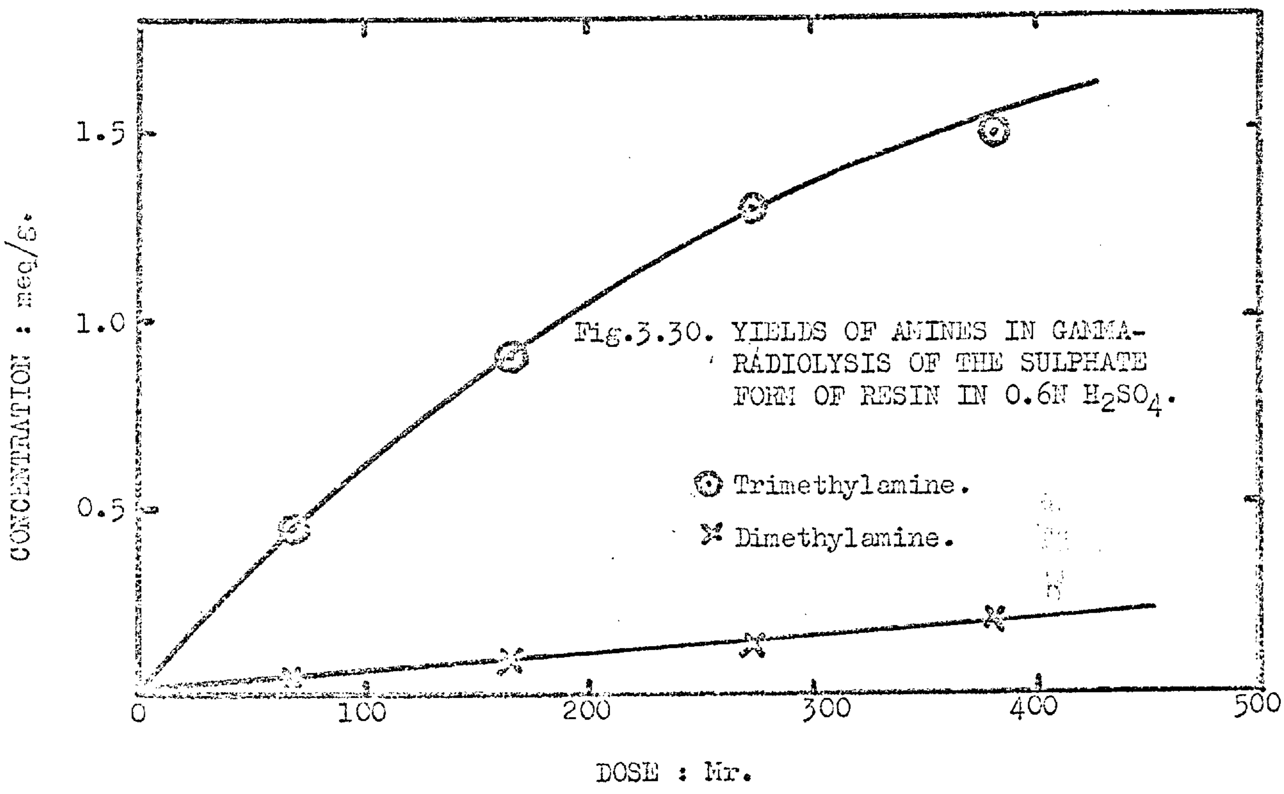


Fig.3.30. YIELDS OF AMINES IN GAMMA-RADIOLYSIS OF THE SULPHATE FORM OF RESIN IN 0.6N H_2SO_4.

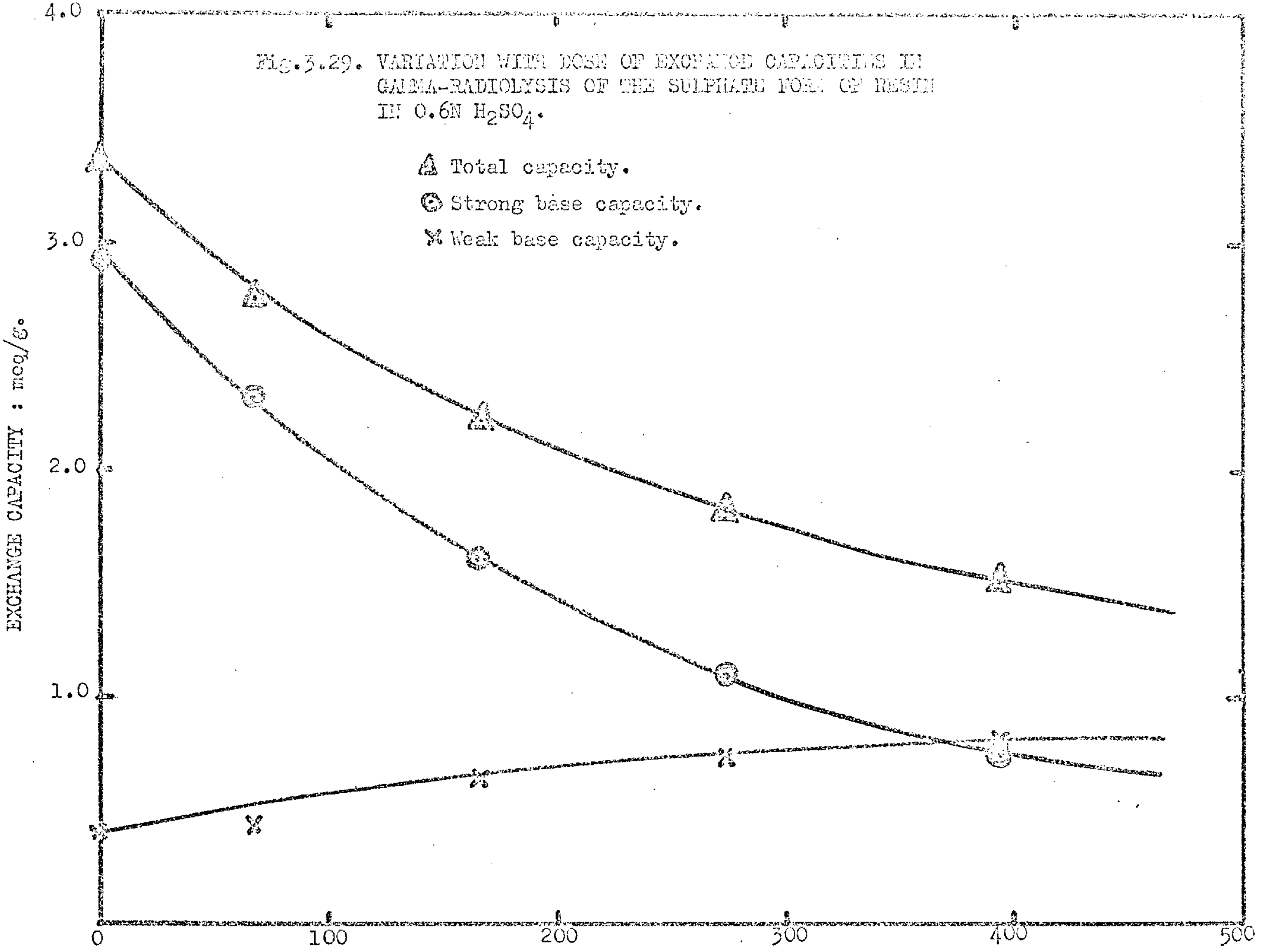


Fig.3.29. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN GAMMA-RADIOLYSIS OF THE SULPHATE FORM OF RESIN IN 0.6N H_2SO_4.

considerably more scission of the N-CH_3 bond occurred in this case compared with the chloride form (GWB in nitrate form is 1.6 and GWB in chloride form is 0.70 at 100 Mr. Table 3.17.). It was also observed that the yields of amines in α-radiolyses for both forms were somewhat less than those expected from capacity changes.

(b) γ-radiolysis of the chloride and sulphate forms of resins.

The yields of trimethylamine and dimethylamine in γ-radiolysis of the chloride and sulphate forms of resins are shown in Figs. 3.28. and 3.30. G(amines) decreased at higher doses as a consequence of the presence of smaller amounts of strong base groups present at such doses. The phenomenon was also observed in the γ-radiolysis of these resins in neutral aqueous media. Over the whole dose range the amine yields are smaller in acid (Table 3.15, 3.16.) than in neutral (Table 3.9. and 3.10.) media, confirming that the rate of γ-radiolysis of these salt forms are reduced by hydrogen ions.

Swelling weights.

(a) Alpha radiolysis of the chloride and nitrate forms of resins.

Alpha radiolysis of both forms of resins in acid media results in continued decrosslinking as the radiation dose is increased (Fig.3.32.). If the swelling weight changes due to

α-radiolysis of the chloride form of resin under the two conditions, e.g. in presence of 0.7N HCl and 10^{-3}N HCl are compared (Figs.3.32. and 3.22.) it is observed that the decrosslinking occurred at somewhat lower rates in the higher acid concentration. On the other hand, the α-radiolyses of nitrate form of resin (Figs.3.11. and 3.32.) show that decrosslinking is slightly greater in higher acid concentration. It seems that the decrosslinking of the resin is also a function of the HNO_3 concentration in the irradiation medium. The radiolytic decomposition products of HNO_3, e.g. NO_2, could enhance the decrosslinking either by secondary reactions or by addition to the radical sites on the polymer preventing the formation of crosslinking(49).

(b) γ-radiolysis of the chloride and sulphate forms of resins in acid media.

The swelling weight changes due to γ-radiolysis of the two salt forms in presence of acids are shown in Fig.3.32. The swelling weight changes of the sulphate form of resin in neutral aqueous medium were shown in Fig.3.22. From comparison of these two figures, it is noted that the sulphate form of resin in acid medium undergoes decrosslinking up to about 175 Mr., while in neutral aqueous medium, the swelling weights remains almost constant up to this dose. However, at higher doses, resin is crosslinked under both the circumstances.

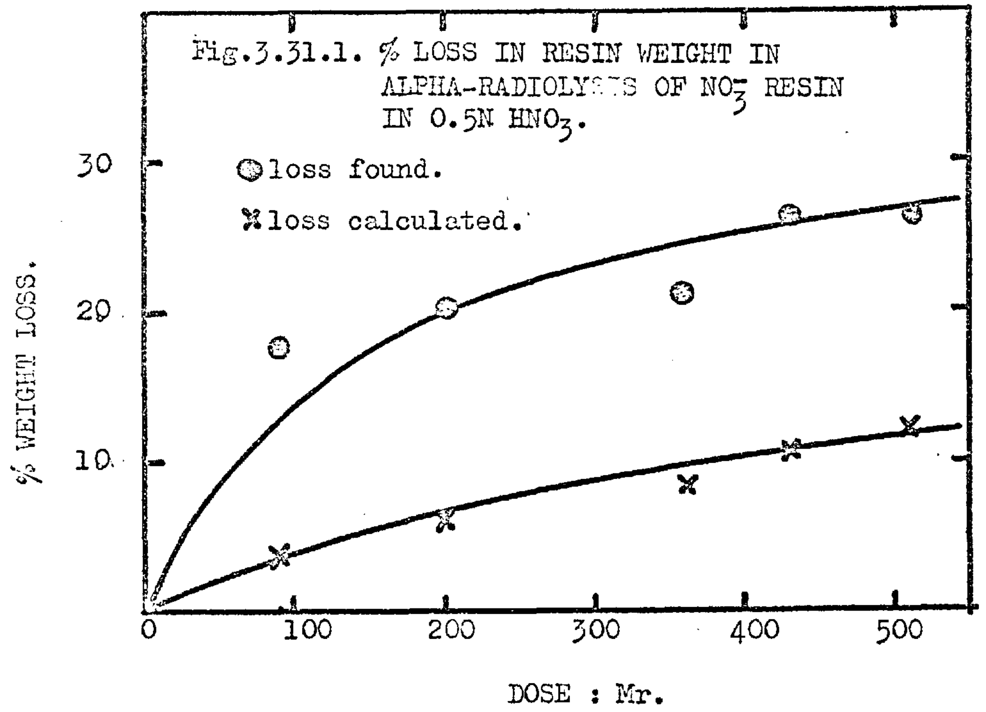


Fig.3.31.1. % LOSS IN RESIN WEIGHT IN ALPHA-RADIOLYSIS OF NO_3^- RESIN IN 0.5N HNO_3.

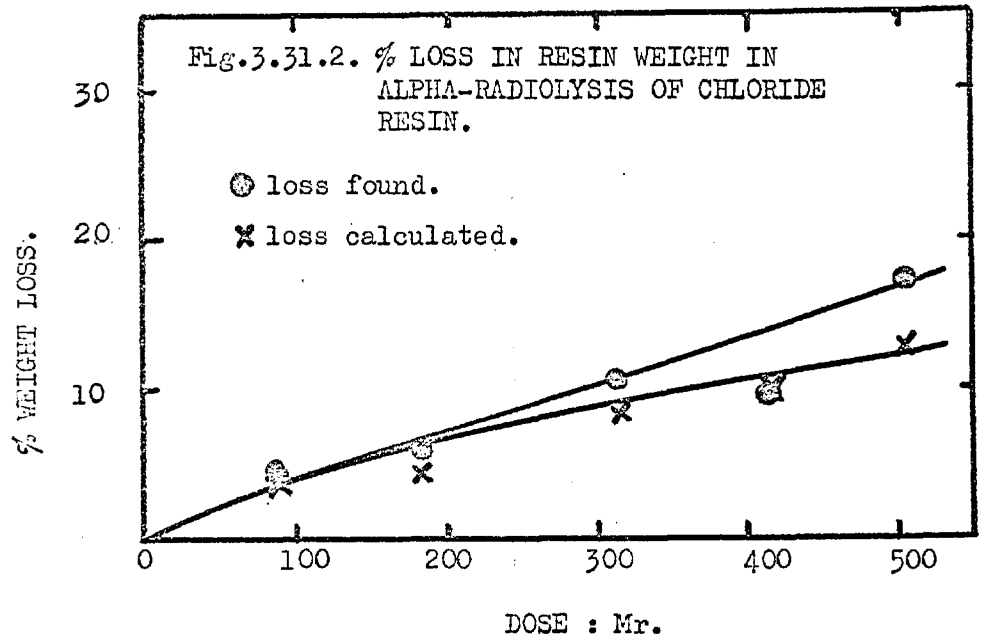


Fig.3.31.2. % LOSS IN RESIN WEIGHT IN ALPHA-RADIOLYSIS OF CHLORIDE RESIN.

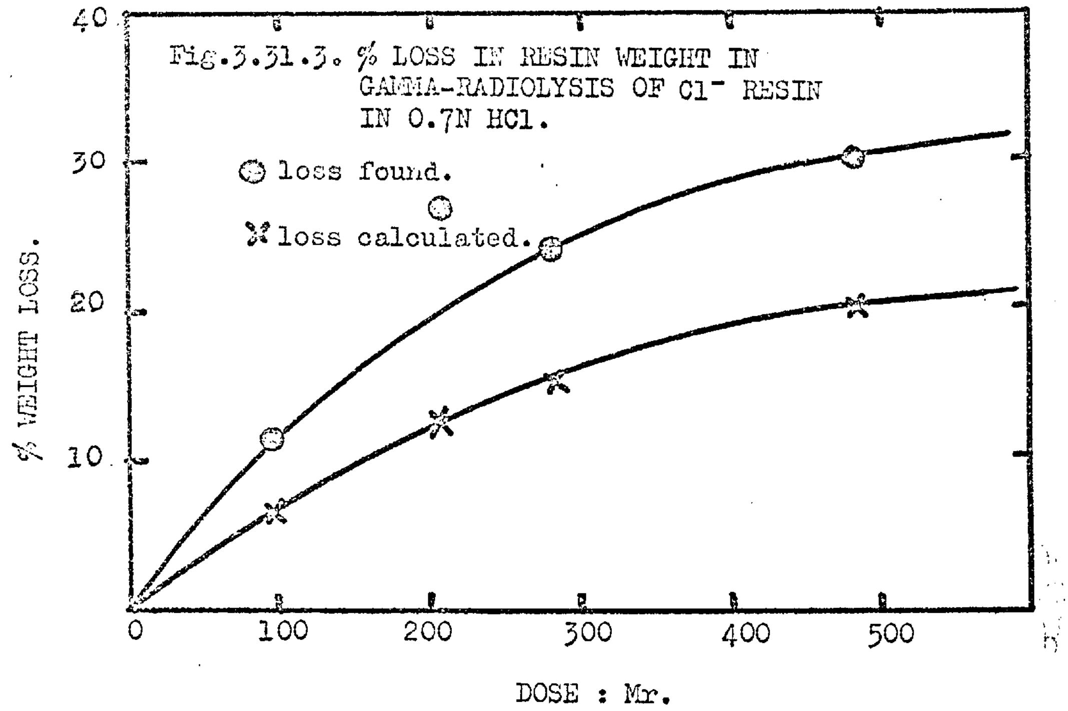


Fig.3.31.3. % LOSS IN RESIN WEIGHT IN GAMMA-RADIOLYSIS OF Cl^- RESIN IN 0.7N HCl.

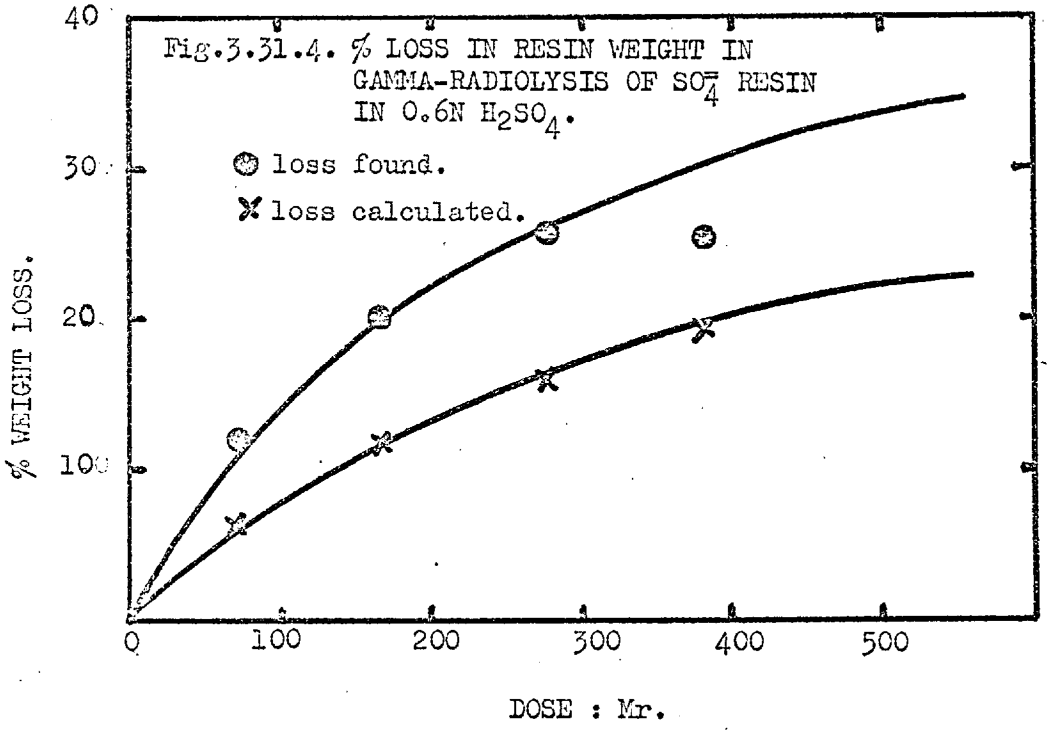


Fig.3.31.4. % LOSS IN RESIN WEIGHT IN GAMMA-RADIOLYSIS OF $SO_4^=$ RESIN IN 0.6N H_2SO_4.

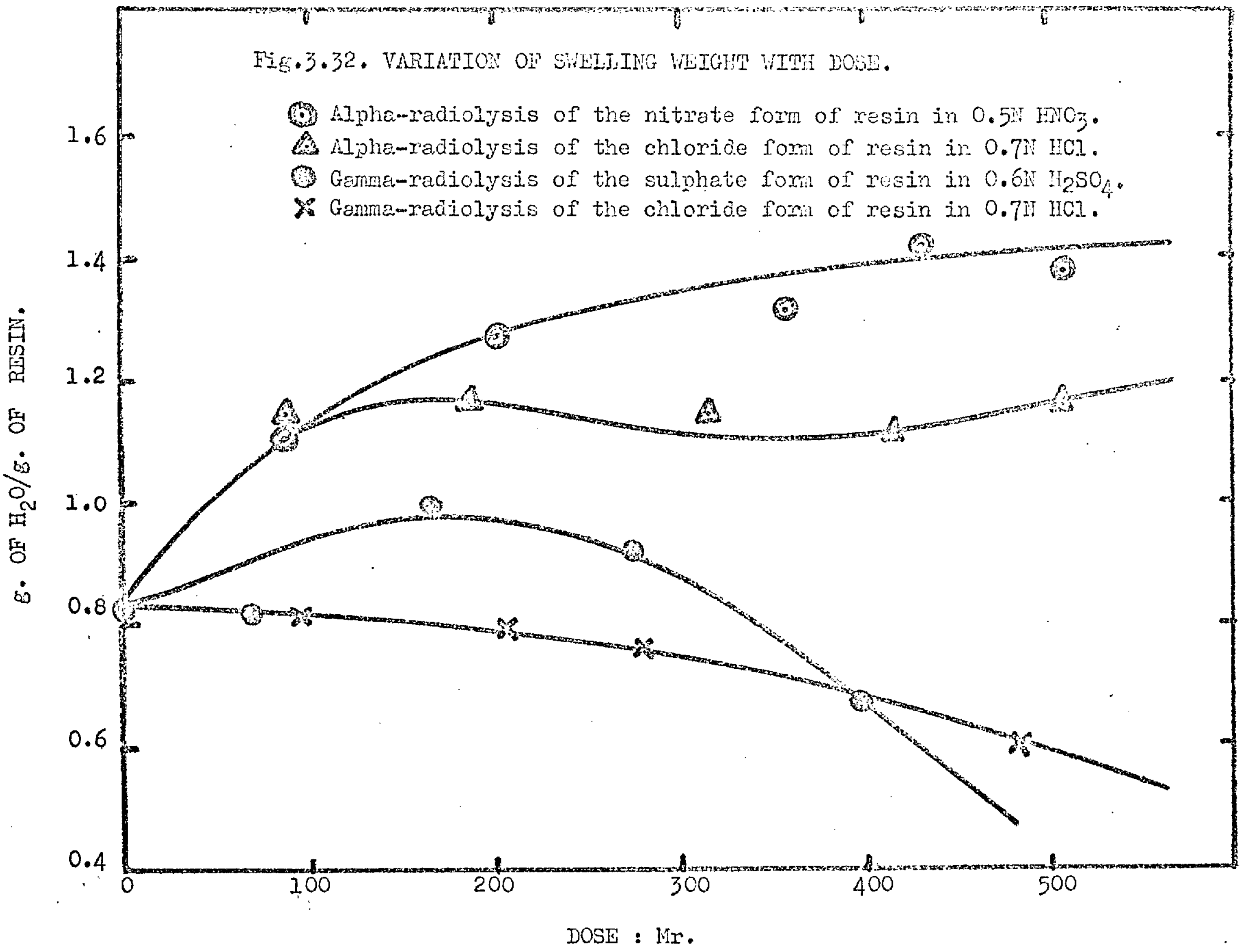


Fig.3.32. VARIATION OF SWELLING WEIGHT WITH DOSE.

Natarajan(16) observed that with the increasing γ-dose on the chloride resin in neutral aqueous medium, the crosslinking is increased, but to a much smaller extent than the hydroxide form. In this work, the swelling weight of the chloride form of resin in 0.7N HCl remains almost constant up to 300 Mr., above which the crosslinking is observable. These results show that the swelling weight changes are not only dependant on the type of radiation or ionic form or concentration of the functional groups left, but also to a small extent on the presence of hydrogen ions. It is also noted that HNO_3 causes decrosslinking of the resin as the dose is increased. It is mainly for this reason that a resin is greatly decrosslinked when irradiated in 7N HNO_3(16).

The swelling weight change is therefore considered to be a complex function of the various factors discussed above.

Weight losses.

Weight losses found after irradiations and weight losses calculated due to the capacity changes are plotted for alpha radiolyses of the chloride and nitrate forms of resins and γ-radiolyses of the chloride and sulphate forms of resins in presence of the respective acids (Fig.3.31.1-4). The major proportions of the weight losses are obviously due to the loss of functional groups. On comparison with Figs.3.20.1-3.21.2 it is noted that the differences between the losses found and losses calculated are higher for acid medium than neutral medium, implying that polymer dissolution is more extensive in the former than the latter. It is interesting to note that alpha radiolysis of the nitrate resin both in 0.5N and in $\sim 10^{-3}$N HNO_3, results in greater weight loss than that found in alpha radiolysis of the chloride resin in 0.7N HCl. Also, the nitrate resin loses more weight when irradiated in higher acid concentration. This increased loss in weight may be explained by the enhanced dissolution of the polymer matrix caused by radiolytic decomposition products of HNO_3. The maximum dissolution of the polymer matrix, in the dose range studied, is found to be 10% of the initial weight of the resin when subjected to γ-radiation in presence of 0.7N acid. The maximum dissolution of the polymer in alpha radiolysis of the nitrate resin in 0.5N HNO_3 is found to be 15% of the initial weight of the resin.

3.3.4. Effects of alpha particle dose rate on the decomposition of anion exchange resins.

In the previous section, the alpha-particle irradiation of Cl^- resin in 0.7N HCl, at a dose rate of 10 Mr. per day, has been discussed. Irradiation of the same resin under similar conditions at a dose rate of 20 Mr/day have been carried out up to 700 Mr. The variation of capacity with dose rates is shown in Fig.3.23. It is thus clear that varying the α-dose rate by a factor of 2 does not bring about any significant change in the rate of decomposition.

Alpha-particle irradiation of nitrate resin in approximately 10^{-3}N HNO_3 at a dose rate of 30 Mr/day have been carried out up to 2100 Mr. (Table 3.19.). The changes in total, strong base and weak base capacities (Fig.3.33.) may be compared with the results of the α-radiolysis of the same resin under the same condition, but at a dose rate of 10 Mr/day. Degradation studies at 30 Mr/day showed that at 650 Mr. 50% of the strong base and 24.5% of the total capacities were lost, while the weak base capacity increased to 25.5% of the total capacity.

Previously it has been shown (Fig.3.9.) that the resin under similar conditions but at a dose rate of 10 Mr/day, lost 45% of strong base capacity at 600 Mr. Apart from an increase in the proportion of weak base capacity produced at the higher dose rate, there was no noticeable difference between the two cases.

Since by varying the dose rate by factors of 2 and 3 could not distinguish any observable dose rate effect, the sulphate resin in 0.7N H_2SO_4 was irradiated by α-particles at a dose-rate of 1.0 Mr/day (previous irradiations having been carried out at 20 Mr/day). The changes in capacities with variation of total dose were measured. Fig.3.35. shows that 50% of the strong base capacity and 34.5% of total capacity were lost at 230 Mr. while the weak base capcity was increased to 15% of the total. It was found that the same resin in 0.7N H_2SO_4 at a dose rate of 20 Mr/day lost 50% strong base and 35% total capacity at 500 Mr., while increase in weak base was 15% of the total, showing that the rate of degradation of the resin was doubled, when the α-dose rate was reduced by a factor of 20. The Table 3.21. shows G-values at 100 Mr. and 500 Mr. for decomposition of Cl^- and NO_3^- resins and at 100 and 250 Mr. for the $SO_4^=$ form of the resin. Comparing the G-values in alpha-radiolysis of $SO_4^=$ resin at 20 Mr/day (Table 3.12.) it can clearly be seen that the rate of decomposition at the lower dose rate was much higher.

Basic Products.

The amine yields from the Cl^- form of the resin were observed to be the same at both 10 and 20 Mr. per day.

The increases of amine yields with increasing dose at dose rates of 10 and 30 Mr. per day in the irradiated nitrate resin followed the same pattern with the exception that $G(CH_3)_3N$ at the higher dose rate was initially slightly less than at the lower dose rate (G = 2.4).

Table 3.18: Alpha particle irradiation of chloride form of resin slurried in 0.7N HCl : variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction.	Corrected capacities meq/g.		$(CH_3)_3N$	$(CH_3)_2NH$	CH_3NH_2	Total volatile base	Swelling weights	% loss in resin weights
	Weak base.	Strong base.	meq/g.	Weak base.	Strong base.	meq/g.	meq/g.	meq/g.	meq/g.	$g.H_2O/g.$	
Nil	0.52	4.10	0.45	0.07	4.55	Nil	Nil	Nil	Nil	0.82	Nil
105	0.80	3.38	0.68	0.11	4.06	0.21	0.07	0.014	0.42	1.05	6.0
202	0.86	3.11	0.60	0.26	3.71	0.52	0.10	0.018	0.61	1.10	9.5
266	0.74	3.00	0.48	0.26	3.48	0.57	0.15	0.020	0.69	1.09	9.0
433	0.92	2.58	0.50	0.42	3.08	0.75	0.18	0.037	0.93	1.09	11.5
695	0.99	1.77	0.43	0.56	2.20	0.86	0.22	0.070	1.10	0.99	12.0

Dose rate of 20 Mr/day.
Chloride resin slurried with $AmCl_3$ solution in 0.7N HCl.

Table 3.19.: Alpha particle irradiation of nitrate form of resin slurried in approximately 10^{-3}N HNO_3 : variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g. Weak base.	Measured capacities meq/g. Strong base.	Capacity correction. meq/g.	Corrected capacities meq/g. Weak base.	Corrected capacities meq/g. Strong base.	$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	Swelling weights g.H_2O/g.	% loss in resin weights.
0	0.26	3.79	0.21	0.05	4.00	Nil	Nil	0.82	Nil
89	0.56	3.10	0.48	0.09	3.58	0.17	0.016	1.14	3.0
256	0.89	2.78	0.59	0.30	3.37	0.44	0.028	0.97	14.0
*415	1.26	1.98	0.60	0.66	2.56	0.86	0.044	1.20	18.0
430	1.22	2.48	0.64	0.58	3.12	0.76	0.048	1.08	17.0
740	1.37	1.04	0.75	0.62	1.79	1.10	0.114	1.26	18.0
*1280	1.79	0.53	0.56	1.23	1.09	1.35	0.175	1.44	30.0
*2100	1.50	Nil	0.32	1.18	0.32	1.28	0.280	1.36	40.0

Dose rate 30 Mr/day.

Niteate resin slurried with $Am(NO_3)_3$ solution in $\sim 10^{-3}$N HNO_3.

*10% of strong base groups in $Am(NO_3)^-$ form.
90% of the strong base groups in NO_3^- form.

Table 3.20: Alpha particle irradiation of sulphate form of resin slurried in 0.6N H_2SO_4: variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction. meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	Swelling weights g.H_2O/g.	% loss in resin weights.
	Weak base.	Strong base.		Weak base.	Strong base.				
0	0.76	2.60	0.30	0.46	2.90	Nil	Nil	0.82	Nil
32	1.98	1.16	1.39	0.58	2.55	0.10	0.029	1.00	9.0
71	1.94	1.02	1.28	0.66	2.30	0.27	0.036	1.13	10.0
115	0.96	1.61	0.46	0.50	2.07	0.40	0.087	1.00	12.0
145	1.47	0.94	0.68	0.80	1.62	0.44	0.120	1.40	20.5
228	1.39	1.00	0.56	0.84	1.56	0.40	0.194	1.25	21.0

Dose rate of 1.0 Mr/day.
Sulphate resin slurried with $Am_2(SO_4)_3$ solution in 0.6N H_2SO_4.

Table 3.21. G-values for decomposition of resin.

Form of Resin	Acidity.	α-particle dose rate Mr/day.	Dose Mr.	-G Total capacity.	-GSB capacity.	+GWB capacity.	$G(CH_3)_3N$
Cl^-	0.7N HCl	20	100	2.7	4.3	0.70	2.9
			500	2.7	3.3	0.70	1.6
NO_3^-	10^{-3}N HNO_3	30	100	2.9	5.0	1.6	2.4
			500	2.5	3.8	1.3	1.7
$SO_4^=$	0.7N H_2SO_4	1.0	100	6.75	8.0	2.9	3.6
			250	2.3	2.9	0.83	1.5

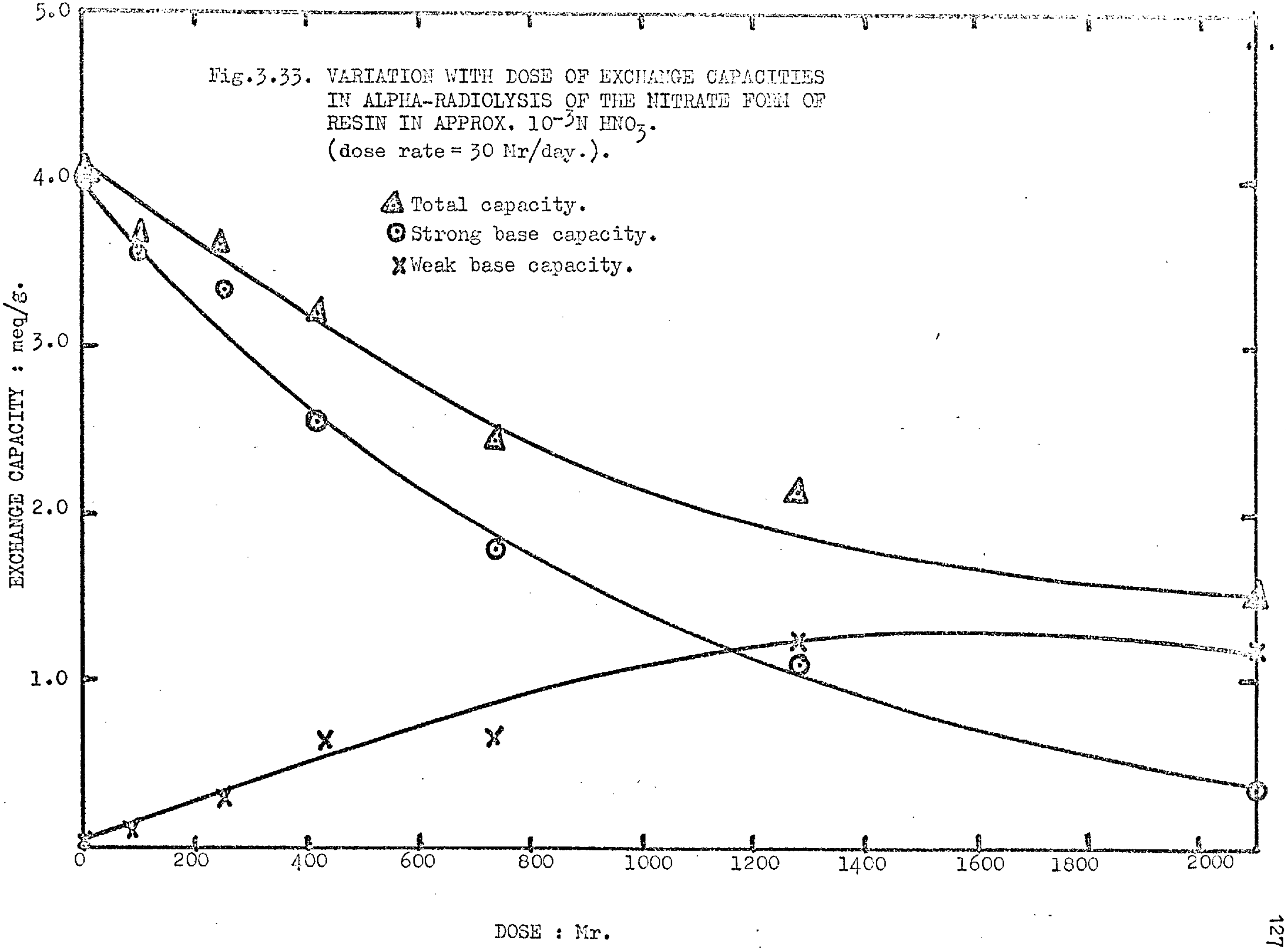


Fig.3.33. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN ALPHA-RADIOLYSIS OF THE NITRATE FORM OF RESIN IN APPROX. 10^{-3}N HNO_3. (dose rate = 30 Mr/day.).

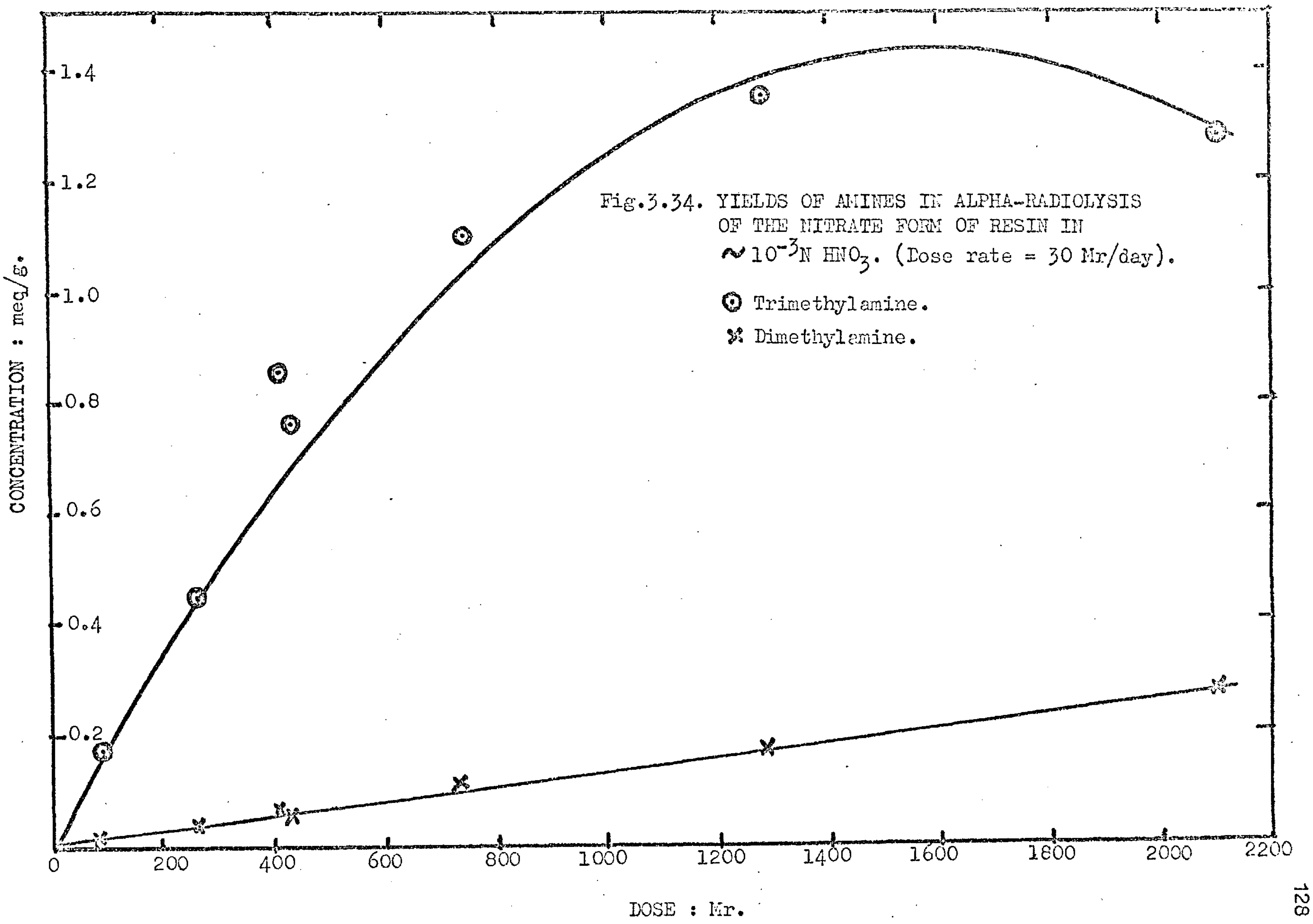


Fig.3.34. YIELDS OF AMINES IN ALPHA-RADIOLYSIS OF THE NITRATE FORM OF RESIN IN $\sim 10^{-3}$N HNO_3. (Dose rate = 30 Mr/day).

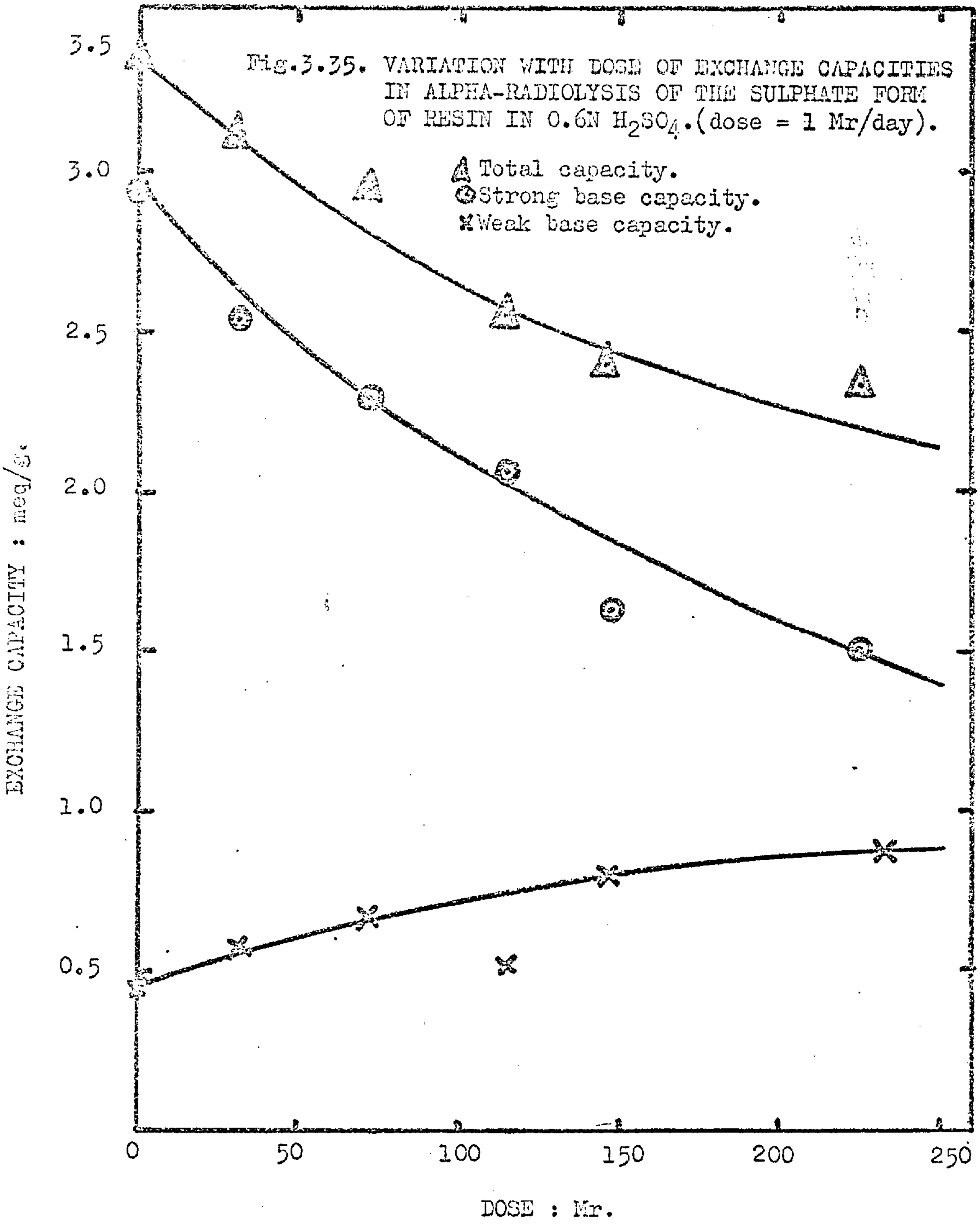


Fig.3.35. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN ALPHA-RADIOLYSIS OF THE SULPHATE FORM OF RESIN IN 0.6N H_2SO_4.(dose = 1 Mr/day).

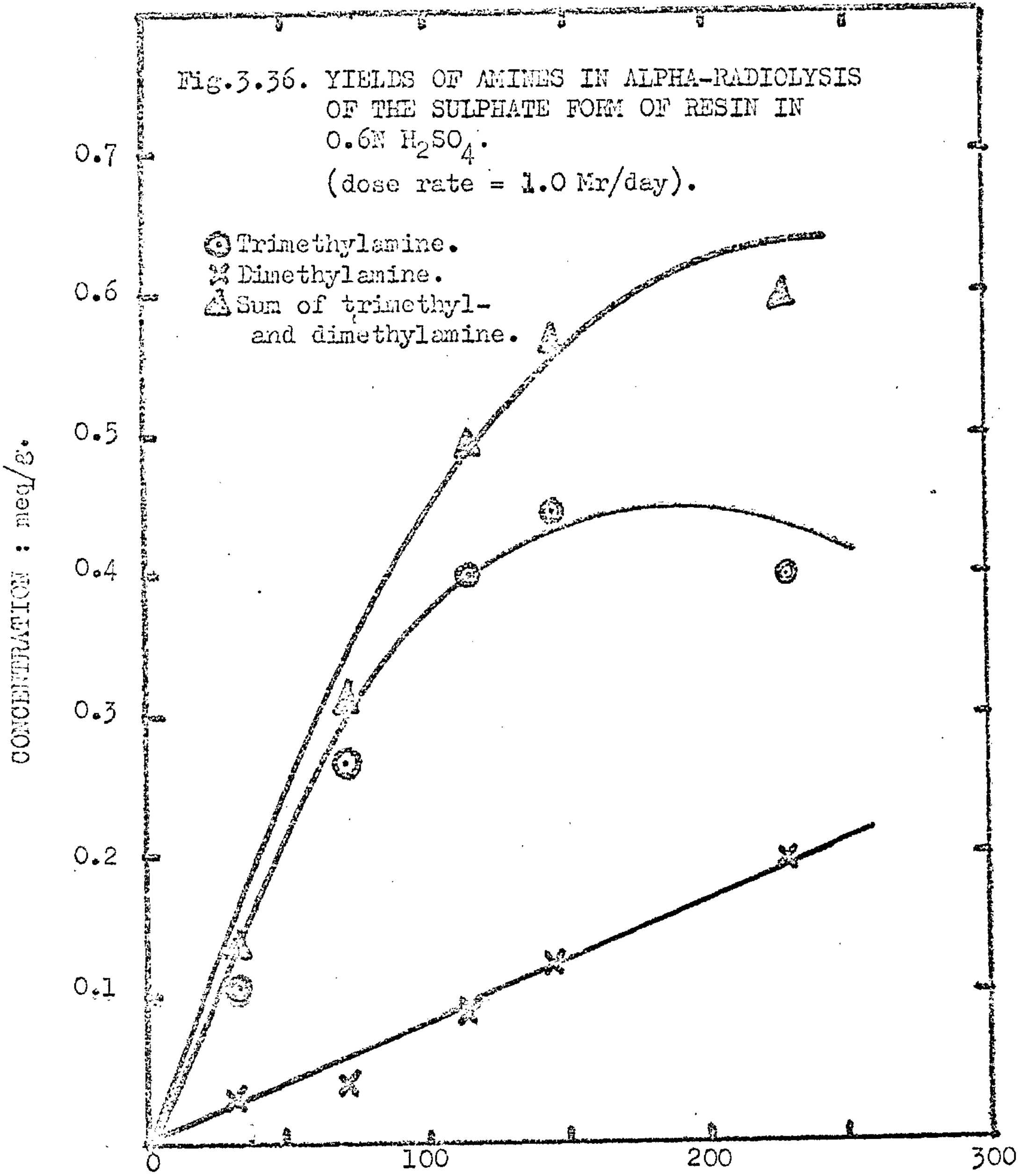


Fig.3.36. YIELDS OF AMINES IN ALPHA-RADIOLYSIS OF THE SULPHATE FORM OF RESIN IN 0.6N H_2SO_4.
(dose rate = 1.0 Mr/day).

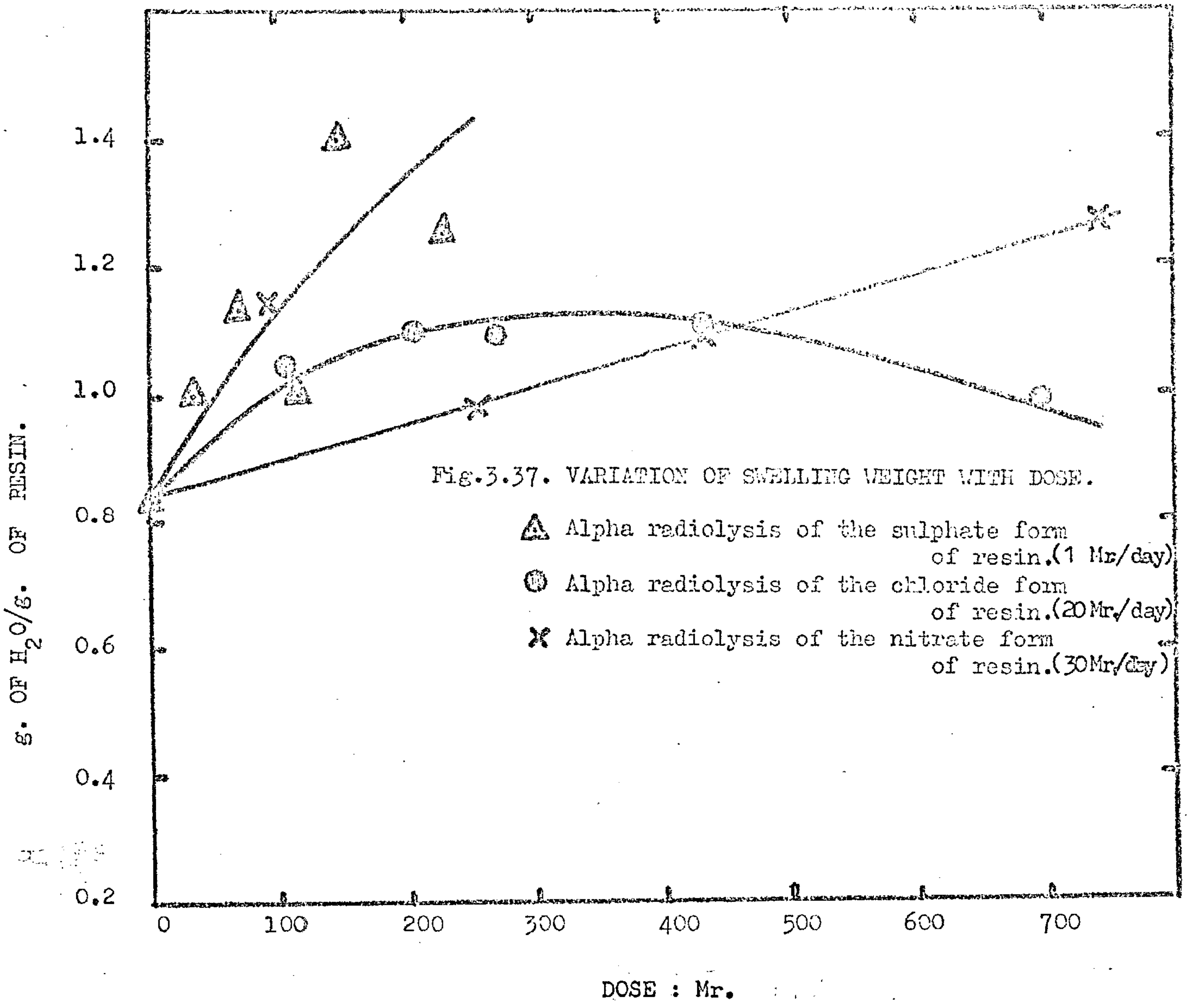


Fig.3.37. VARIATION OF SWELLING WEIGHT WITH DOSE.

As the dose rate variations in alpha radiolyses of both chloride and nitrate forms of resin were small (factor of 2 and 3), the variations in the yields of products were small and it was difficult to distinguish any dose rate effect. Alpha radiolysis of the sulphate form of resin at a dose rate of 1 Mr/day, however, shows considerably higher yields of both trimethyl- and dimethylamine (Fig.3.36) compared with those at a dose rate of 20 Mr/day. (Fig.3.15).

Plots of trimethylamine and the sum of trimethyl and dimethylamine against dose show that the yield of basic products increased with increasing dose. $G(CH_3)_3N$ at 100 Mr. dose was found to be 3.6, which was considerably higher than that found at 20 Mr. per day (2.9). (Tables 3.21. and 3.12.). It was also observed that above 150 Mr., there is a nett destruction of trimethylamine resulting in an increased production of dimethylamine when a lower dose, i.e. 1 Mr/day was employed. This shows that the secondary decomposition of the trimethylamine is also enhanced by a lower dose rate.

Swelling weights

Changes in swelling weights of chloride, nitrate and sulphate forms of resins at dose rates of 20, 30 and 1 Mr/day respectively are plotted in Fig.3.37. The swelling weight changes of these resins at other dose rates are given in Figs. 3.32, 3.11. and 3.22. respectively. It is observed that the decrosslinking rate is slightly reduced at higher dose rates. At a very low dose rate (in $SO_4^=$ resin irradiation at 1 Mr.) decrosslinking appears to occur to a greater extent.

It may thus be concluded that from changes in capacities, amine yields and swelling weights an effect of dose rate was clearly observed in the α-radiolysis of the sulphate form of resin, when the dose rate was varied by a factor of 20. The rate of decomposition was highest at the lowest dose rates.

3.3.5. Radiation-induced decomposition of dried resins.

The effects on resin stability, of absorbed heavy ions, different counter ions, acidity and dose rate have now been discussed. It was considered that radiation stability is also likely to depend on whether or not water is present during irradiation. For this purpose, alpha-particle irradiation of dried thiocyanate and γ-irradiations of thiocyanate (Table 3.22) and chloride resins have been carried out.

Capacity changes

(a) Alpha radiolysis of dry thiocyanate resin.

The capacity changes and product yields of alpha radiolysis of the dried thiocyanate form of resin with absorbed americium are given in Table 3.22. Fig.3.38. shows that 50%

Table 3.22 : Alpha particle irradiation of dried thiocyanate form of resin : variation with dose of exchange capacities, yields of amines and swelling weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction. meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	CH_3NH_2 meq/g.	Swelling weights. $g.H_2O/g.$
	Weak base.	Strong base.		Weak base.	Strong base.				
0	0.46	3.50	0.15	0.31	3.65	Nil	Nil	Nil	0.82
95	0.90	2.31	0.30	0.60	2.81	0.30	0.06	-	0.70
215	1.00	2.16	0.30	0.70	2.46	0.58	0.13	0.08	0.68
440	1.29	1.20	0.47	0.83	1.67	0.90	0.21	0.08	0.69
600	1.33	0.79	0.46	0.87	1.25	1.12	0.23	0.07	0.75
790	1.00	0.65	0.36	0.64	1.01	1.24	0.27	0.07	0.48

5% of the strong base groups in $Am(SCN_4)^-$ form.

95% of the strong base groups in SCN^- form.

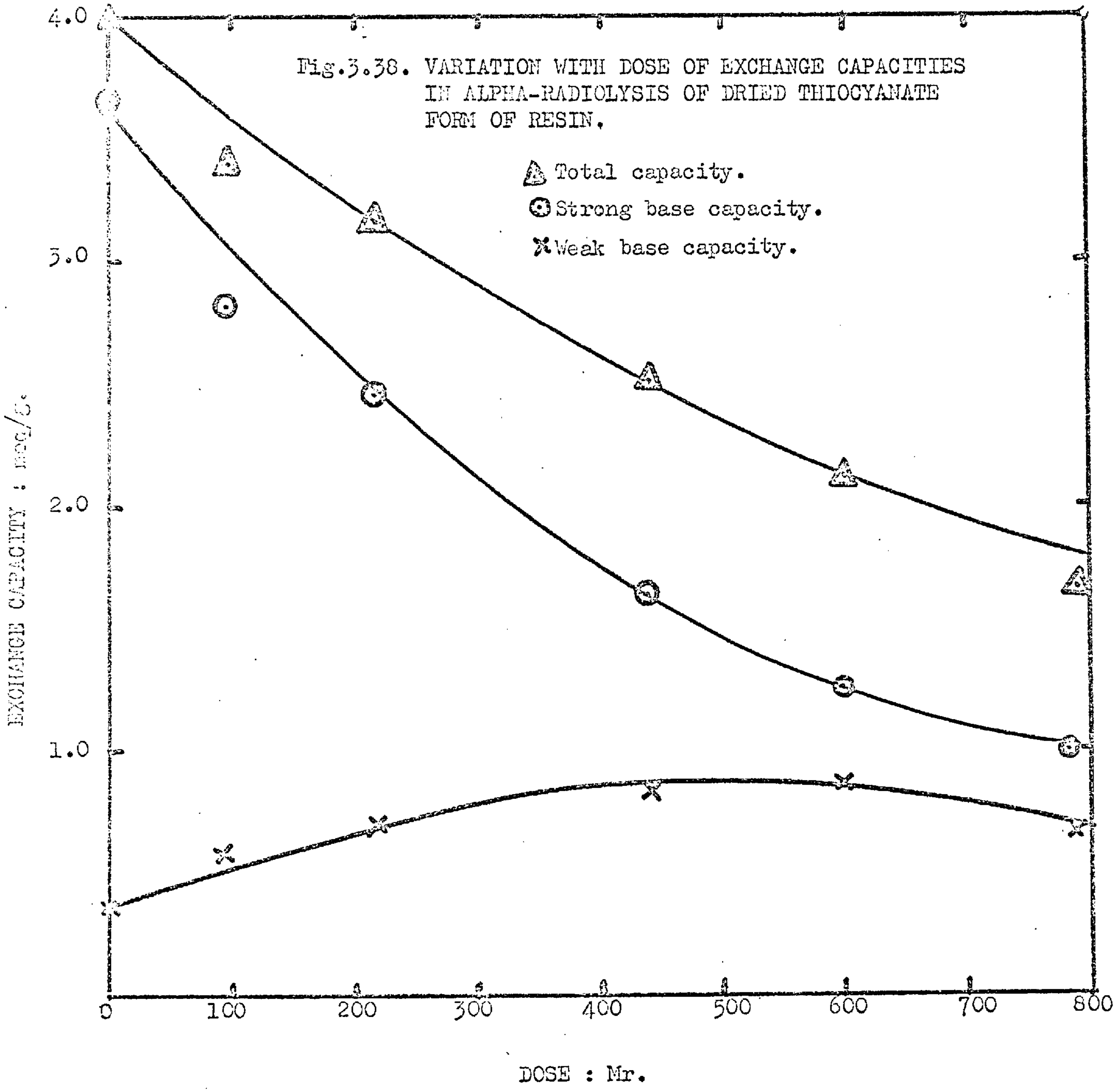


Fig.3.38. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN ALPHA-RADIOLYSIS OF DRIED THIOCYANATE FORM OF RESIN.

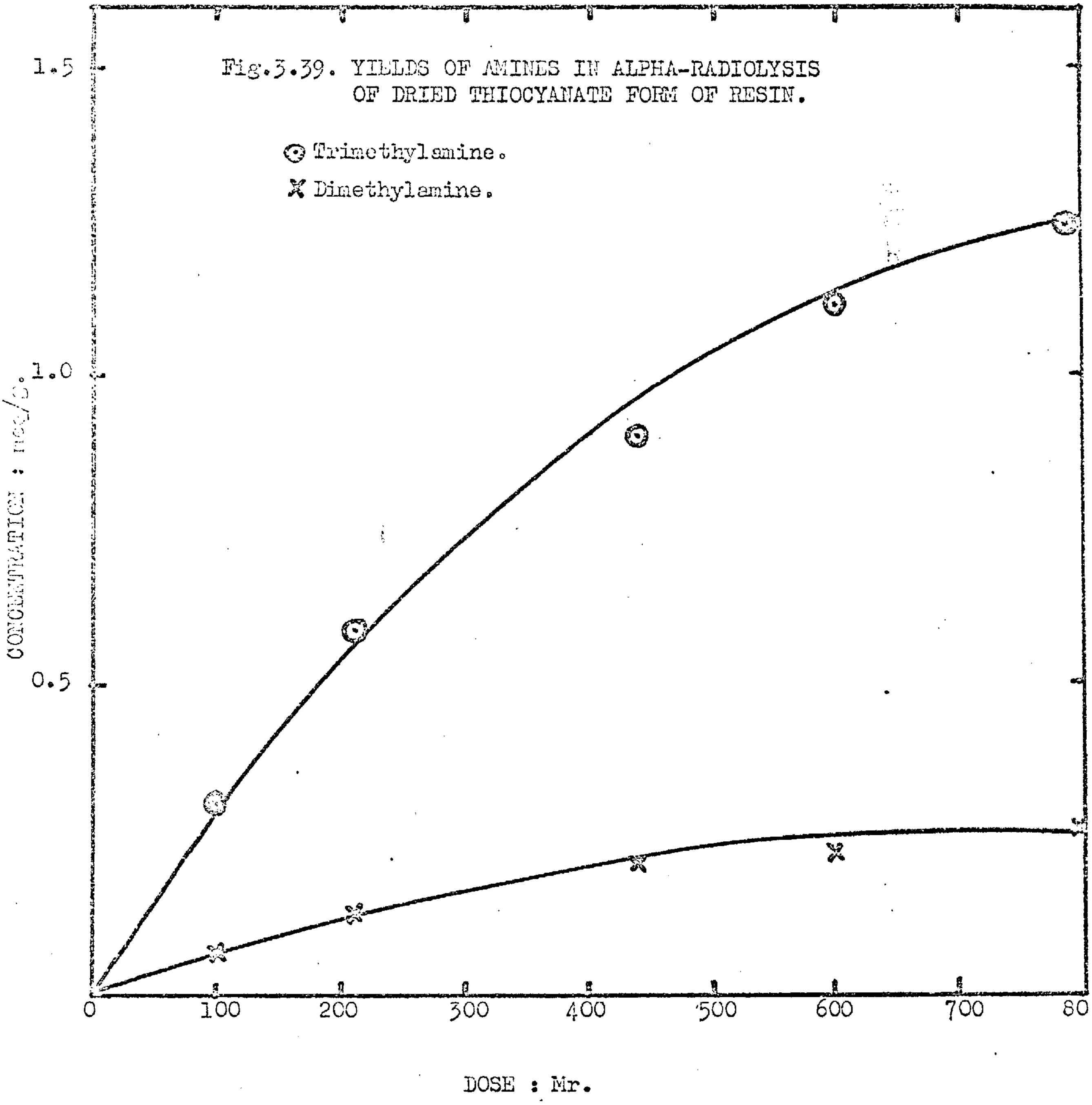


Fig.3.39. YIELDS OF AMINES IN ALPHA-RADIOLYSIS OF DRIED THIOCYANATE FORM OF RESIN.

of the strong base is lost at 375 Mr. At this dose the total capacity loss of the resin is 33% and there is an increase in weak base capacity equal to 12% of the total capacity. With the same resin slurried in 5M NH_4SCN, alpha radiolysis produced a similar percentage strong base capacity loss at the lower dose of 250 Mr. (Fig.3.1.). Figs. 3.1. and 3.38 also show that the gain in weak base capacity was greater for wet resin.

The total capacity changes in both wet and dried resin are almost the same; 50% of the total capacities being lost at 600 and 650 Mr. respectively. These results indicate that the wet resin is more unstable than the dry resin, as far as strong base groups are concerned.

(b) γ-radiolysis of dry thiocyanate resin.

γ-radiolysis of the dried thiocyanate form of resin shows that 50% of the strong base capacity is lost at 375 Mr. In section 3.3.1., Fig.3.5., it was shown that the wet thiocyanate resin lost 50% strong base capacity at 250 Mr. These show that the resin is more stable in the absence of water. It is also observed that in wet resin, the growth in weak base capacity is greater than in the dry resin.

(c) γ-radiolysis of the dried chloride form of resin.

Table 3.24. and Fig.3.42. show the results of the γ-radiolysis of the dried chloride form of resin. The resin in absence of water loses 50% of its strong base capacity at 365 Mr. This is comparable with γ- and alpha radiolysis of the thiocyanate form of resin. The slurried chloride form of resin lost 50% of strong base capacity at 215 Mr. (Fig.3.16) showing that a resin is more stable in absence of water. Table 3.25. shows the G-values of the capacity changes at 100 and 500 Mr. indicating the rates of decomposition at initial and higher doses. It was noted that these dried resins contained about 6-7% H_2O and it is likely that this water content may have brought about the slightly higher G-values of the capacity changes than those expected from absolutely dry resin. However, the effects of the variable water content in the radiolyses of resins have been more extensively investigated and are reported in the next chapter.

Basic Products.

Fig.3.39. shows the increase of trimethylamine with increasing alpha dose up to 800 Mr. Dimethylamine is produced at a considerably high rate up to about 200 Mr., above which the rate of production is reduced presumably because of its part decomposition to monomethylamine. It may be noted that

Table 3.23: Gamma irradiation of dried thiocyanate form of resin : variation with dose of exchange capacities, yields of amines and swelling weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction. meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	Swelling weights. $g.H_2O/g.$
	Weak base.	Strong base.		Weak base.	Strong base.			
0	0.58	3.33	0.22	0.36	3.55	Nil	Nil	0.82
145	0.57	2.43	0.17	0.40	2.60	0.59	0.029	0.73
220	0.83	2.10	0.30	0.53	2.40	0.78	0.030	0.74
320	0.57	1.80	0.23	0.34	2.03	0.98	0.033	0.70
350	0.67	1.65	0.16	0.51	1.81	1.10	0.035	0.70
450	0.70	1.35	0.18	0.52	1.53	1.20	0.036	0.65
570	0.70	1.33	0.17	0.53	1.50	1.28	0.036	0.60

Table 3.24: Gamma irradiation of dried chloride form of resin : variation with dose of exchange capacities, yields of amines, swelling weights and % loss in resin weights.

Dose Mr.	Measured capacities meq/g.		Capacity correction. meq/g.	Corrected capacities meq/g.		$(CH_3)_3N$ meq/g.	$(CH_3)_2NH$ meq/g.	Swelling weights. g.H_2O/g.	% loss in resin weights.
	Weak base.	Strong base.		Weak base.	Strong base.				
0	0.50	3.45	0.15	0.35	3.60	Nil	Nil	0.82	Nil
95	0.66	2.80	0.21	0.45	3.01	0.43	0.07	0.79	1.5
170	0.70	2.43	0.18	0.52	2.61	0.67	0.15	0.79	2.0
284	0.77	1.88	0.27	0.51	2.14	1.03	0.23	0.78	12.0
473	0.77	1.32	0.18	0.59	1.49	1.43	0.33	0.70	15.0

Table 3.27. G values for decomposition of dried resins.

Resin.	Dose Mr.	-G Total.	-G(strong base)	+G(weak base)	$G(CH_3)_3N$
Thiocyanate form α-radiolysis	100	3.8	5.5	1.9	2.9
	500	3.0	3.8	1.0	2.0
Thiocyanate form γ-radiolysis	100	4.6	4.9	0.30	4.1
	500	3.7	3.8	0.30	2.8
Chloride form γ-radiolysis	100	4.8	5.8	0.96	4.1
	500	3.8	4.2	0.34	2.8

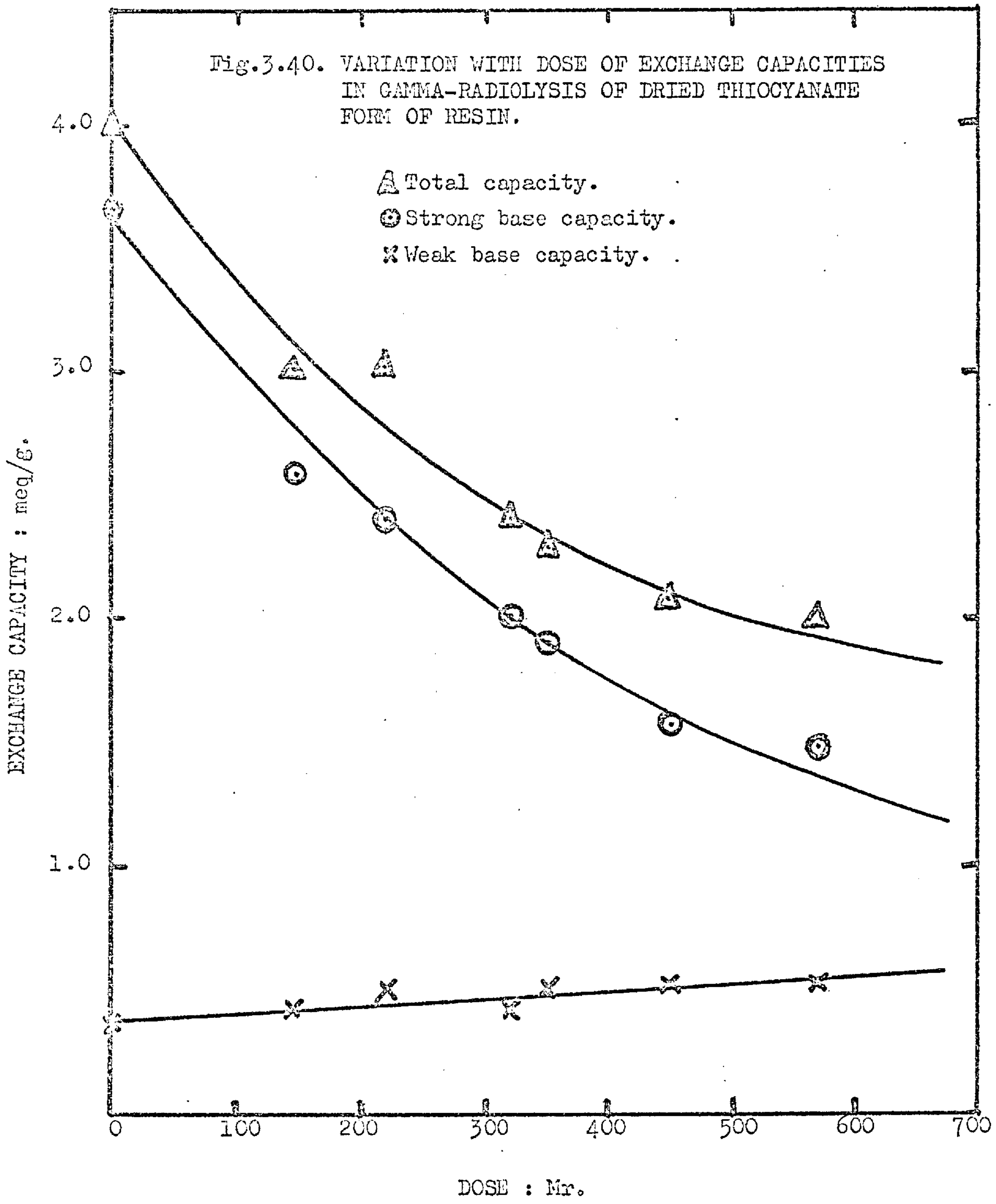


Fig.3.40. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN GAMMA-RADIOLYSIS OF DRIED THIOCYANATE FORM OF RESIN.

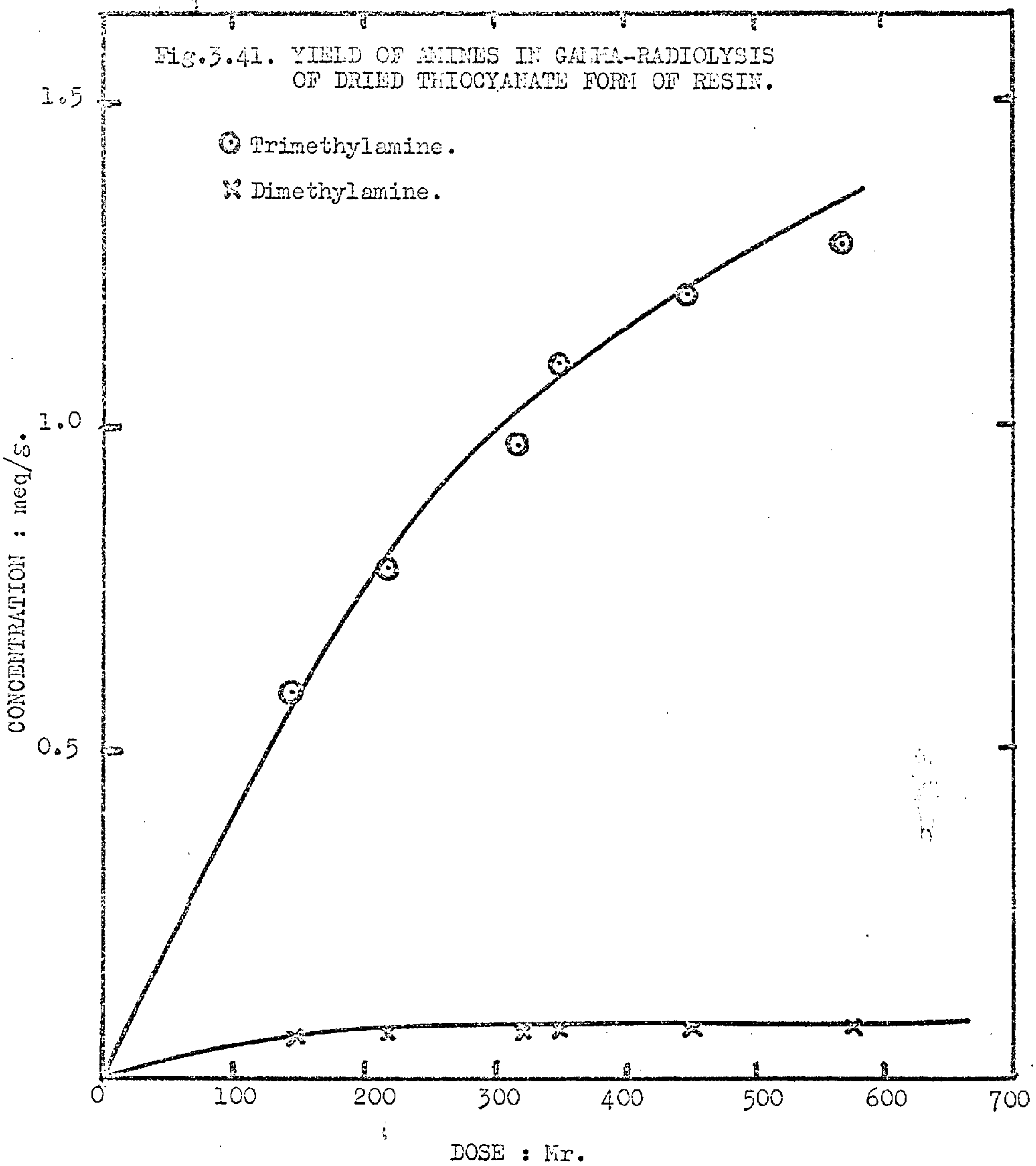


Fig.3.41. YIELD OF AMINES IN GAMMA-RADIOLYSIS OF DRIED THIOCYANATE FORM OF RESIN.

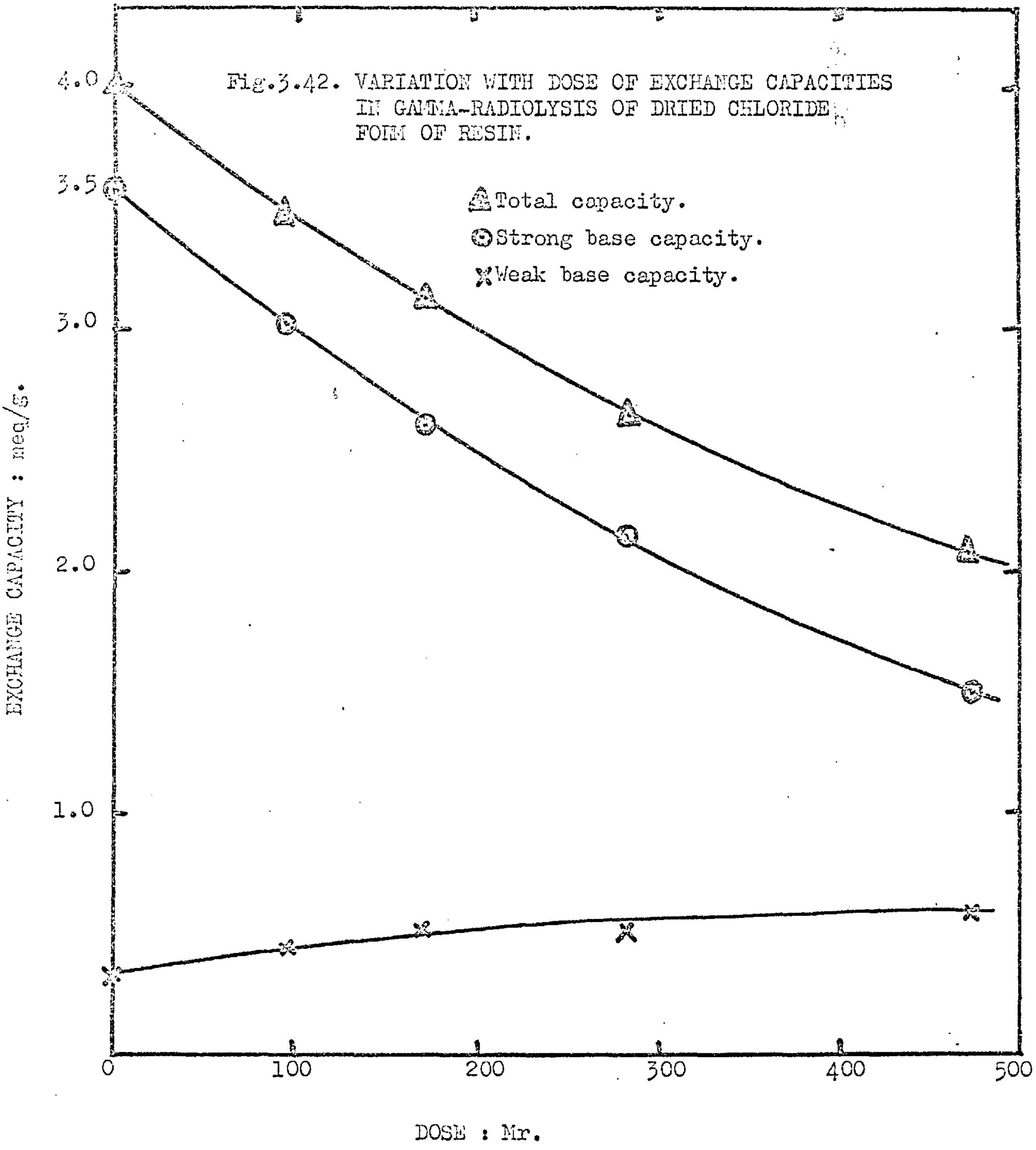


Fig.3.42. VARIATION WITH DOSE OF EXCHANGE CAPACITIES IN GAMMA-RADIOLYSIS OF DRIED CHLORIDE FORM OF RESIN.

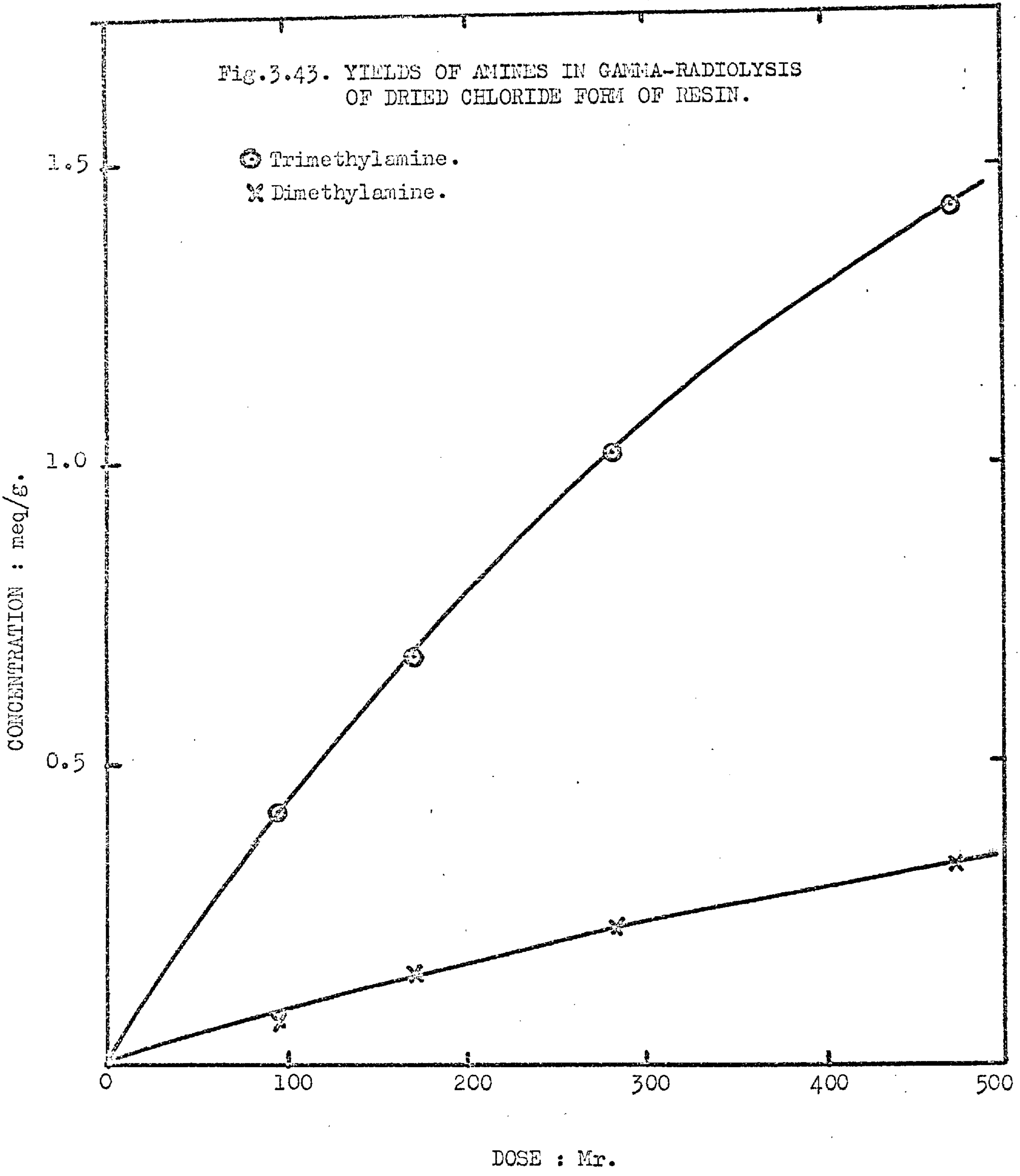


Fig.3.43. YIELDS OF AMINES IN GAMMA-RADIOLYSIS OF DRIED CHLORIDE FORM OF RESIN.

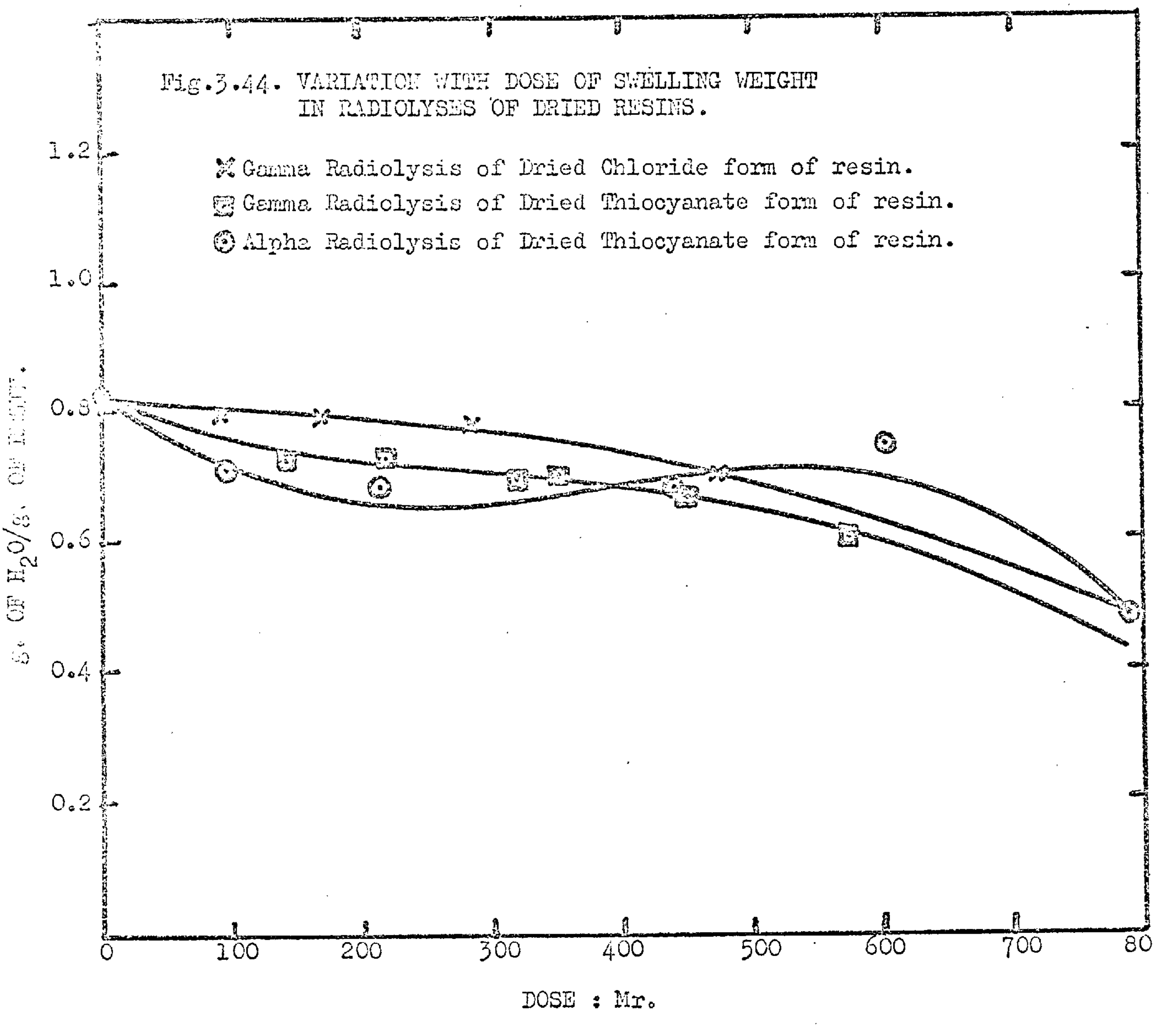


Fig.3.44. VARIATION WITH DOSE OF SWELLING WEIGHT IN RADIOLYSES OF DRIED RESINS.

the ratio of dimethylamine to trimethylamine is higher than that found in alpha particle irradiations of slurried resin. Since the weak base production in dried resin was found to be less than that in wet resin, the dimethylamine yield should have been also less in the former. It thus indicates that most of the dimethylamine in dry state possibly resulted from trimethylamine decomposition and it is not understood why the trimethylamine decomposition by alpha particle was greater in absence of water.

(b) γ-radiolysis of dry thiocyanate and chloride forms of resins.

The yield of trimethylamine with increasing γ-dose on dry thiocyanate form of resin is shown in Fig.3.41. The dimethylamine yield is found to be much less than that in the alpha radiolysis of the dry resin. It has already been noted that in γ-radiolysis, the weak base production is lower than in wet resin and consequently the contribution of dimethylamine from weak base radiolysis is also low. It also appeared that γ-radiolysis of the dried resin essentially decomposed the strong base functional groups to produce trimethylamine.

The yields of trimethyl- and dimethylamines in γ-radiolysis of dried chloride resins are shown in Fig.3.43.

The amine yields are found to be much lower in the dry resin than the wet resin (Fig.3.19.) . For example, the sums of the trimethyl- and dimethylamine yields in dried and slurried chloride forms of resins at 100 Mr. are 0.5 meq/g. and 0.85 meq/g. respectively. It is thus clear from both capacity changes and product yields that a resin is more unstable in presence of water than when dry.

Swelling Weights.

Changes in swelling weights are shown in Fig.3.44. for alpha radiolysis of the dried thiocyanate and γ-radiolysis of the dried thiocyanate and chloride forms of resins. The swelling weight changes in alpha radiolyses of the thiocyanate form of resin were found to be similar in both dry and wet conditions and indicate an increase in crosslinking as irradiation proceeds. Crosslinking appears to occur at slower rate in the dry resin (cf. Fig.3.11.).

The dried chloride form shows a decrease in swelling weight with increasing γ-radiation dose. Examination of Fig. 3.44. shows that the rate of decrease in swelling weight is very small and it is likely that little crosslinking occurs in the dry resin; the slight fall being mainly due to loss in functional groups which results in less water of hydration in the irradiated resin.

CHAPTER 4.

DIRECT AND INDIRECT EFFECTS OF γ-RADIATION UPON ANION EXCHANGE RESINS.

4.1. Introduction.

Published data(15-24, 43-50) on the radiation induced decomposition of ion exchange resins are often conflicting and their interpretation is difficult due to lack of knowledge of the mechanisms involved. Nater(46) and Natarajan(16) concluded that direct absorption of energy excites the valence electron system in an anion exchange resin resulting in the rupture of C-N bonds. Several workers(44, 48, 49, 50) however indicated that decomposition may occur through radicals produced by radiolysis of water. Similar conflicting views in radiation-induced decomposition of cation exchange resins are prevailing. Posek et al(20) consider that functional groups break down by direct absorption of energy, while Natarajan(16) suggests that indirect action is possibly responsible for the decomposition of cation exchange resin functional groups. Rahman and Clay(60) have made a study of the reaction mechanism involved and explain the radiation-induced decomposition of cation exchange resins by means of $\cdot OH$ radical reactions.

In this work, it has been demonstrated (Section 3.3.1. to 3.3.5.) that degradation of the anion exchange resins by γ-radiolysis is higher than that caused by alpha radiolysis when the resin is subjected to the same dose. In alpha radiolysis, indirect action can play comparatively little part in the decomposition due to radical-radical reactions along the radiation track and the major portion of the decomposition may be due to direct action. On the other hand, γ-radiolysis may cause the decomposition of anion exchange resins both by direct and indirect actions and it is possibly due to this that the degradation is found to be higher in γ-radiolysis compared to alpha radiolysis of a resin slurry. Indeed, the reduction in the extent of degradation in presence of acid (Section 3.3.3.) compared to radiolysis in presence of water (Section 3.3.2.) also suggest the possibility of indirect action in γ-radiolysis of resin slurries . It is also established (Section 3.3.5.) that the slurried resin decomposes to a greater extent than the dried resin, suggesting that radiolytic products of water play some part in the decomposition of slurried resins.

In the present investigation, experiments have been designed to evaluate the roles of direct and indirect actions in bringing about the decomposition of anion exchange resins. The roles of H_2O^-, .OH and H. have been studied by irradiating the anion exchange resins with variable water contents and in presence of different scavengers. A qualitative study of the UV-light de-amination of an anion exchange resin has also been made in an attempt to understand the importance of excitation processes involved.

4.2. Experimental.

4.2.1. Irradiation.

The chloride, nitrate and sulphate forms of resins have been irradiated by cobalt-60 γ-rays at a dose rate of $5.0\text{x}10^{19}$ ev/g.hr. (19.5 Mr/day) up to a total dose of $3.0\text{x}10^{20}$ ev/g., under the following conditions.

Irradiation condition	Form of resin
i) Dry resin.	Chloride, nitrate and sulphate.
ii) Neutral aqueous media.	Chloride, nitrate and sulphate.
iii) Variable water content in the resin.	Chloride.
iv) Slurried with N_2O solution under 20 lbs/in.^{2}.	Chloride.
v) Slurried with sodium nitrate solutions of variable concentrations.	Chloride.
vi) Slurried with ethanol solutions of variable concentrations.	Sulphate.

The resins have been prepared by the methods described in 2.2.3.. All these resins were dried at 80°C. for 5 hours. It was found to be important not to employ higher temperature for drying the resins in order to avoid even the slight decomposition that occurs at 105°C. (Section 2.2.3). Even so the small amount of trimethylamine present in the resin was determined by washing a 2.0 g. sample of dried resin with distilled water and estimating the amine by the picrate method(55). This value was subtracted from the amine estimated after the irradiation of the resin.

Irradiation with variable water content.

The initial water content of the resin dried at 80°C. was determined by further drying a known weight of the resin at 105°C. to a constant weight; the 80°C.-dried resin was found to contain 4% water. The composition of the resin-water mixture was then adjusted to 1:0.30 ratio by equilibrating the resin with water vapour, at room temperature, in a desiccator containing water, for 2 days. Occasional mixing of the resin sample in the desiccator helped to bring about an uniform absorption of water. Higher compositions of resin : water, e.g. 1:0.70 and 1:1 were made by adding a known quantity of water to the dry resin and mixing them in a mechanical shaker in a closed vessel. The mixtures were left for 10 days so that the distribution of water in the resin became uniform. The highest resin : water ratio (1:1.5) was obtained by adding a known quantity of water to a weighed sample of dried resin, the amount of water being just sufficient to soak the resin.

The samples were introduced to the irradiation vessel through a narrow glass tube extended from a B-7 cone, in order to avoid resin sticking to the wall of the vessel during transfer.

Irradiation in presence of N_2O.

2.0g. of the resin were transferred to a glass vessel fitted within a pressure vessel. The latter was fabricated in stainless steel and fitted with inlet and outlet valves and a pressure gauge(61). 10 ml. of water were added to the resin sample. The pressure vessel was closed and N_2O gas was fed at atmospheric pressure through the gas inlet extended to within the resin slurry. After 5 minutes, the outlet valve was closed and the pressure of the N_2O gas was gradually increased up to 20 lbs./in^2. The gradual increase of pressure avoided the splashing of the slurry up the wall of the vessel. The pressure gauge indicated that the pressure remained constant during the irradiation. The irradiations were carried out at a dose rate of $5x10^{18}$ ev/g./hr. up to a dose of $1.2x10^{20}$ev/g.

At the end of an irradiation, the N_2O gas was released through the outlet valve and the solution containing the amine was separated from the resin by filtration and washing. The filtrate and washings were made to a known volume and analysed for trimethylamine.

Irradiation of slurried resins.

1.0 g. resin samples were irradiated as a slurry in 4.0 ml. of water or the following solutions; acid solutions of up to 7N, $NaNO_3$ solution up to 2N and ethanol solution up to 5N.

In the chloride resin—$NaNO_3$ system, some chloride ions from the resin exchanged with nitrate ions from the solution. The mixture was left overnight for equilibrium to be reached and then irradiated at a dose rate of 5.0×10^{19} ev/g/hr. up to 3.0×10^{20} ev/g. After the irradiation, the solution was separated from the resin by filtration. The chloride estimation in the filtrate gave the amount of nitrate ions exchanged into the resin phase and also the amount left in the solution phase.

Dose rate.

The chloride form of resin was irradiated as a slurry in water at dose rates of 5.0×10^{19} and 4.0×10^{18} ev/g/hr.

Irradiation by UV-light.

Two samples of aqueous slurry of the chloride form of resin were contained in B-14 test tubes, one being wrapped externally with black paper. Both were kept at the same distance (10 cm.) from the UV-source for the same period of time and the temperature in both the samples noted.

Trimethylamine was analysed in (i) water washings of the unirradiated resin, (ii) in the resin sample wrapped with black paper and (iii) in the sample exposed to UV-light. Irradiation of the resin in the blackened tube provided a blank for assessing any thermal formation of trimethylamine resulting from the heating from the UV-lamp.

Since glass absorbs most of the UV-light, the resin slurry was also irradiated in a 1 cm. silica cell whilst 4 cm. silica cell containing saturated sodium chloride solution was used to filter out light $\nless$ 2000Å.

The increase in the yield of trimethylamine with time was noted and the effect of the filter was also observed. No actinometry was carried out and consequently it was not possible to evaluate the results quantitatively.

4.3. Results and Discussion.

The result of the γ-radiolysis of the mixtures of chloride form of resin and water are shown in Fig. 4.1.

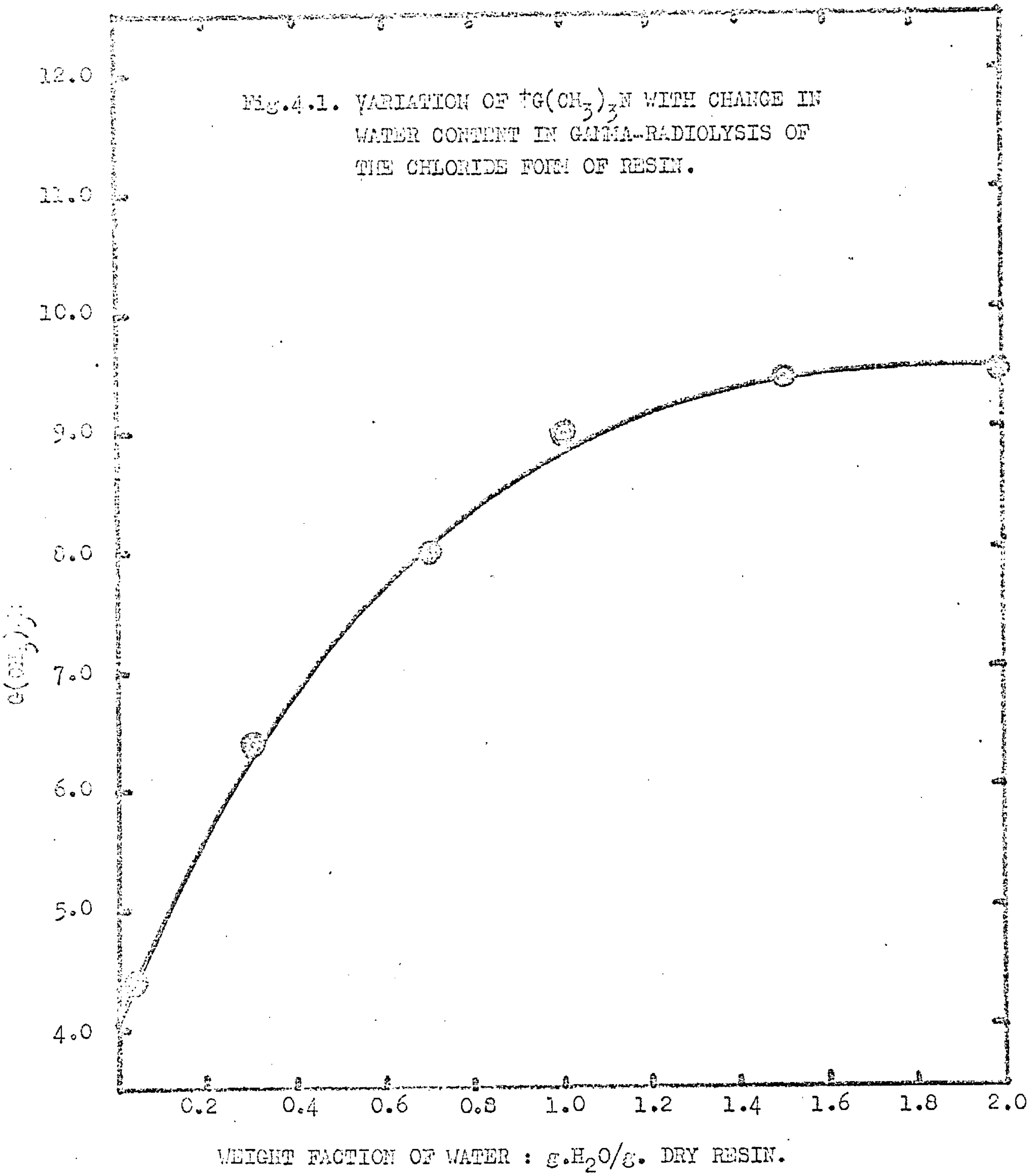


Fig.4.1. VARIATION OF †$G(CH_3)_3N$ WITH CHANGE IN WATER CONTENT IN GAMMA-RADIOLYSIS OF THE CHLORIDE FORM OF RESIN.

The yields of trimethylamine were calculated on the basis of 1g. dry resin and the G-values calculated from the energy absorbed by the resin only, so that any change in G-value with increasing H_2O : resin ratio may be attributed to the indirect effect brought about by the radiolytic decomposition of water. The G-values of trimethylamine have been plotted as a function of weight fraction of water in the resin. If only energy absorbed by the resin was effective in producing trimethylamine, the G-values would have remained constant with increasing water content. But the experimental results show that $G(CH_3)_3N$ increased from $\simeq$ 4.0 (extrapolated value) to 9.5. This marked increase can only be explained on the basis that irradiated reactive intermediates produced from water are capable of reacting with resin to produce trimethylamine. At low water contents a high proportion of the intermediates must so react but at higher water : resin ratios an increasingly high proportion of the energy absorbed by water will be ineffective in producing trimethylamine because of the increasing formation of intermediates at positions remote from resin. It thus appears that more than half of the total decomposition is brought about by the intermediates produced from the radiolysis of water, while the remaining may be attributed to the direct action.

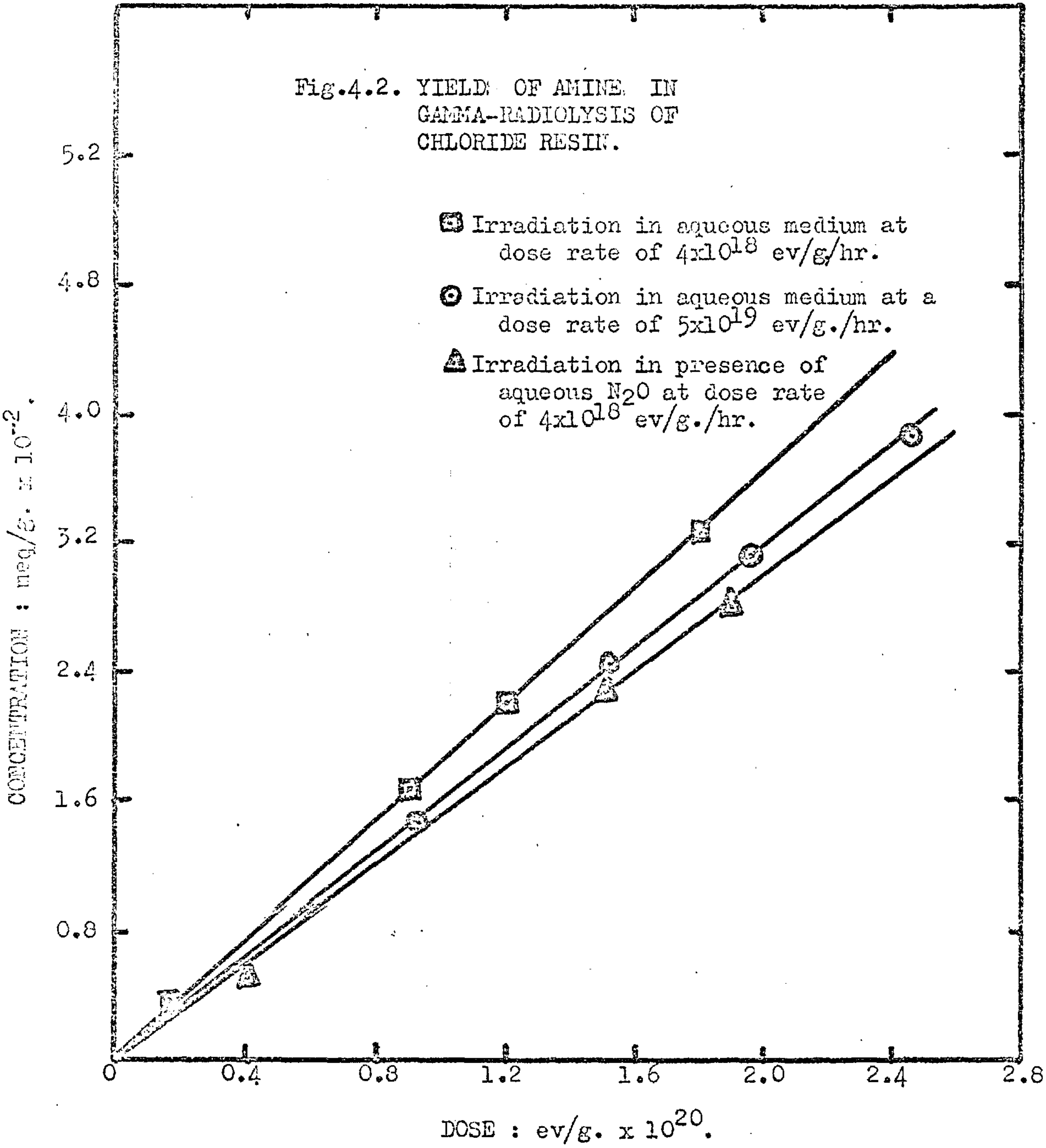


Fig.4.2. YIELD OF AMINE IN GAMMA-RADIOLYSIS OF CHLORIDE RESIN.

It may also be mentioned that if the radicals are responsible for de-amination of the resin, then at a very high dose rate, decomposition would be expected to occur to a smaller extent than that at low dose rates, due to the overlapping of the spurs and thus increasing the chances of radical recombinations. In the present work this was observed to a small extent when the chloride form of resin was irradiated at $3.5\text{x}10^{18}$ and $5\text{x}10^{19}$ ev/g./hr. (Fig.4.2.).

The radiolysis of water is currently assumed to be described by

$$H_2O \rightsquigarrow H., \; .OH, \; H_2O^-, \; H_2, \; H_2O_2.$$

and the effects of radiation on the solutes in aqueous solutions may be ascribed to reactions involving one or more of these species. The $G(CH_3)_3N$ for aqueous slurry of Cl^- resin at a dose rate of $4\text{x}10^{18}$ ev/g.hr. is 10.8. When the same resin was irradiated in the presence of N_2O at 20 p.s.i., the $G(CH_3)_3N$ was found to be 8.86. The concentration of N_2O achieved was fairly low. This small but definite reduction in 'G' may be explained in terms of scavenging of H_2O^- by N_2O

$$H_2O^- + N_2O \longrightarrow N_2O^- + H_2O \qquad \text{... (1)}$$

competing with

$$H_2O^- + R\,N^+(CH_3)_3 \longrightarrow R. + N(CH_3)_3 \qquad \text{... (2)}$$

H^+ is also known to be an efficient scavenger of H_2O^- ($k = 2.36\text{x}10^{10}$ litre/mole sec.)(63).

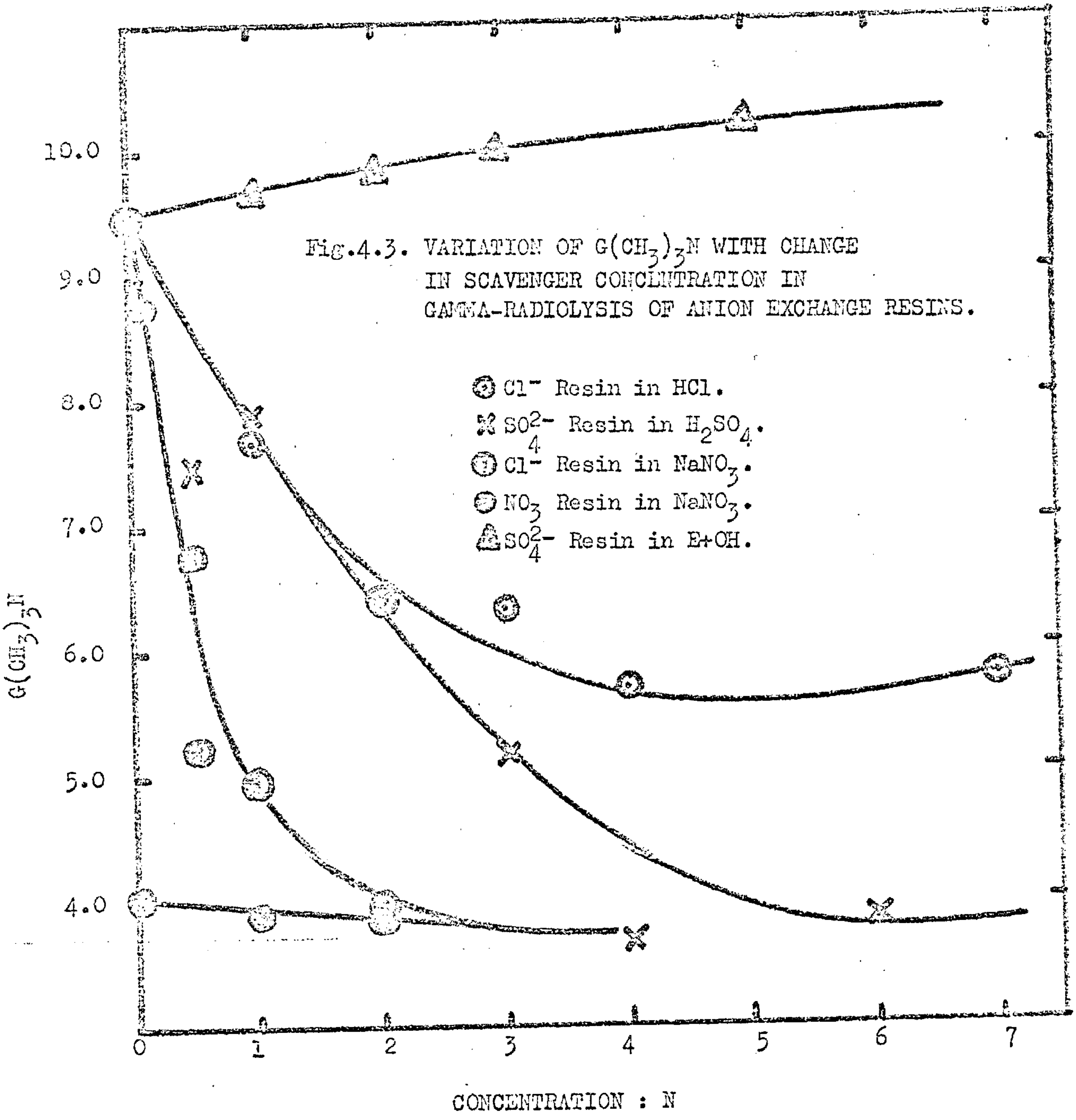


Fig.4.3. VARIATION OF G$(CH_3)_3N$ WITH CHANGE IN SCAVENGER CONCENTRATION IN GAMMA-RADIOLYSIS OF ANION EXCHANGE RESINS.

The efficiency of this species was studied by varying the concentration of HCl used for slurrying the chloride form of resin, from 0-7N. A decrease in $G(CH_3)_3N$ from 9.5 to 5.8 (Fig.4.3.) was observed and this reduction is explained by the reaction of H_2O^- with H^+.

$$H_2O^- + H^+ \longrightarrow H. \qquad \ldots (3)$$

thus reducing the extent of reaction (2).

The minimum G-value observed for maximum scavenging by H^+ is still higher than that found for dry resin ($G \sim 4$). However .OH radicals are known to react with Cl^- ions in acid solution:

$$.OH + Cl^- + H^+ \longrightarrow Cl. + H_2O \qquad \ldots (4)$$

and possibly the Cl. atom produced is capable of bringing about some de-amination.

If however the Cl. atoms are partly responsible for de-amination, these complications can be avoided by use of H_2SO_4 solution as a scavenger for H_2O^- during the radiolysis of the sulphate form of resin. Fig.4.3. shows that increasing concentration of H_2SO_4 decreased the $G(CH_3)_3N$ to a minimum of 3.66. This value is almost equal to the $G(CH_3)_3N$ found for dry resin (Fig.4.1., extrapolated G 4.0), suggesting that most of the indirect formation of $(CH_3)_3N$ is brought about by reaction (2).

It may be mentioned that the formation of trimethylamine from the nitrate form of the resin is not influenced by the presence of water. That is to say that water behaves merely as an inert diluent and $G(CH_3)_3N$ remains constant whether irradiated as dry or slurried resin. This comparative stability of the nitrate form of resin has also been observed by Natarajan(16). The stability of the nitrate form of resin can now be seen to be explicable on the basis of the protection of the resin by nitrate ions against attack by hydrated electrons produced from water, for nitrate ions are known to react efficiently with this species(64). This has been demonstrated by irradiating the chloride form of the resin slurried with $NaNO_3$ solutions of different concentrations. Under these circumstances, some of the chloride ions on the resin were replaced by nitrate ions. Fig.4.3. shows that $G(CH_3)_3N$ in these systems decreased as the concentration of nitrate ions was increased and G $\simeq$ 4.0 was obtained when only 67% of the resin was in the nitrate form. Conversion of the remaining groups to the nitrate form did not bring about any further reduction in the G-value. This disposes of the possibility that stability of the nitrate form is due to the stabilisation of the carbon-amino group bond by nitrate ions rather than protection by successful competition of these ions for hydrated electrons.

$$H_2O^- + NO_3^- \longrightarrow NO_3^{2-} + H_2O.$$

It is interesting that $G(CH_3)_3N$ observed for the dry resin in sulphate, chloride and nitrate forms are similar ($G = 4.0 - 4.6$). Thus the direct radiation stability of the resin does not appear to depend upon the salt form.

The above experiments have shown that H_2O^- is responsible for indirect trimethylamine formation. The roles of other species, e.g. .OH and H. have been investigated by irradiating the sulphate form of resin in the presence of ethanol. Both .OH and H. are known to react efficiently with ethanol(65).

$$.OH + CH_3CH_2OH \longrightarrow CH_3\ \dot{C}H\ OH + H_2O$$

$$H. + CH_3CH_2OH \longrightarrow CH_3\ \dot{C}H\ OH + H_2$$

Fig.4.3. shows that no decrease in $G(CH_3)_3N$ was observed when the resin was irradiated in a slurry with ethanol solution. On the contrary, there was a small increase in $G(CH_3)N$. This rules out the possibility of any reaction of .OH and H. in bringing about the de-amination of the resin.

The role of excitation process in de-aminating the resin was qualitatively tested by exposing the resin-water slurry to UV-light. Fig.4.[illegible] shows that decomposition of the functional group of the resin is a direct function of time of exposure.

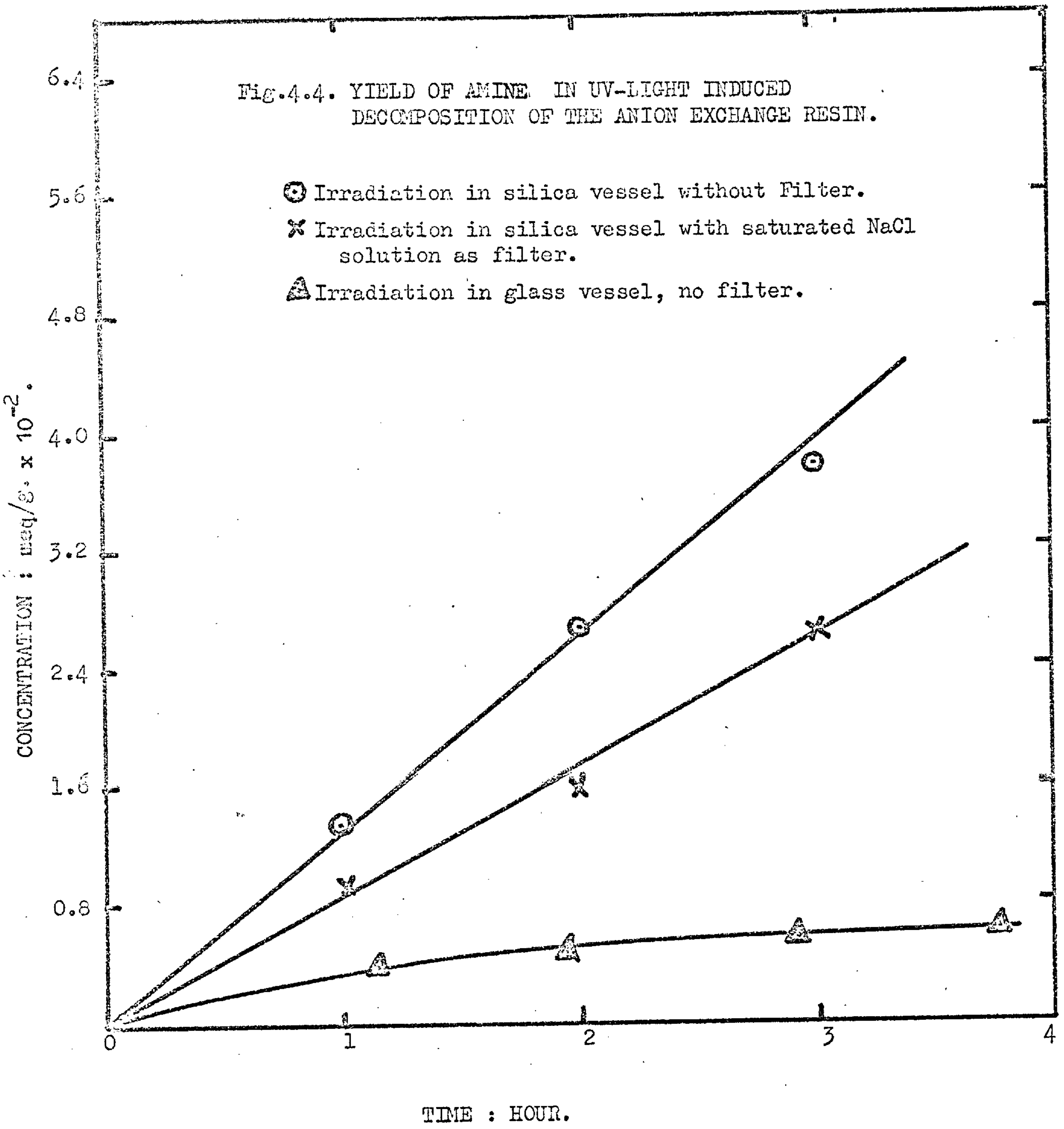


Fig.4.4. YIELD OF AMINE IN UV-LIGHT INDUCED DECOMPOSITION OF THE ANION EXCHANGE RESIN.

Since UV-light is not capable of producing H_2O^-, deamination is considered to be brought about by excitation processes. It is therefore probable that decomposition of dried resin by γ-radiation occurs through the excitation processes.

All the above experiments show the existence of both direct and indirect effects in radiation induced deamination of the anion-exchange resin. The G-value for deamination of the resin slurried with water is ~9.5. When water is absent, the G-value is reduced to ~4.0 (Fig.4.1.). The minimum G-value obtained in presence of H_2O^- scavangers is ~3.7 (Fig.4.3.). No reduction in the G-value is observed when the resin is irradiated in presence of the .OH and H. scavanger. It is therefore concluded that the only species responsible for indirect effect is H_2O^- and ~60% of deamination occurs through the reaction

$$RCH_2\overset{+}{N}(CH_3)_3 + H_2O^- \longrightarrow RCH_2\cdot + N(CH_3)_3 + H_2O$$

and the remaining ~40% through the excitation process.

CHAPTER 5.

CONCLUSIONS.

An important factor in reprocessing of nuclear reactor fuels is the radiation damage to process reagents. Tributylphosphate, an organic compound useful in solvent extraction when subjected to radiation produces hydrolytic products deleterious in a solvent extraction process(66). Exposure of ethylenediamine to more than 0.1 watt-hr. per ml. radiation results in decreasing effectiveness of material as a complexing agent for metallic ions(66). Ion-exchange methods for processing of radioactive solution are attractive and have been proposed for homogeneous reactors(67) and for separation of plutonium from uranium(3, 68). The loss of capacity and changes in swelling weights are the two most important factors affecting the application of ion-exchange resins for radiochemical processing at high activity levels.

The present work shows that γ-radiation causes about twice as much damage to salt forms of Deacidite-FF anion exchange resins as α-radiation. Alpha radiation, in general, causes a 50% loss in strong base capacity at a dose of 500-600 Mr. and of this 50%, 25-30% change is due to scission of $C\text{-}N(CH_3)_3$ bonds and 20-25% change to scission of $N\text{-}CH_3$ bonds.

Gamma radiation usually causes 50% loss in strong base capacity at a dose of 200-250 Mr. and, at this dose, 35-40% of the loss in strong base capacity occurs by scission of $C-N(CH_3)_3$ bonds and the remaining 10-15% is due to scission of $N-CH_3$ bonds.

The anion **resin** decomposition can thus be represented by the following equations

$$RCH_2N(CH_3)_3 \longrightarrow RCH_2\cdot + N(CH_3)_3 \qquad \ldots (1)$$

$$RCH_2N(CH_3)_3 \longrightarrow RCH_2NH(CH_3)_2 + CH_3\cdot \qquad \ldots (2)$$

Reaction (1) is responsible for total capacity loss while (2) shows the conversion of strong base to weak base capacity.

It is established in this work that about 60% of the total capacity loss by γ-radiation is brought about by an indirect action through H_2O^-. The difference between alpha and gamma radiation effects in aqueous resin slurries is due to the large contribution of indirect effect in the gamma radiolysis. It is probable that the nature and extent of the damage brought about by alpha and gamma direct effects is similar. The unusual stability of the resin nitrate to gamma radiation is explained by the electron scavanging action of nitrate ions which prevents or retards those deamination processes occurring through H_2O^- attack.

Dose rate effects in the decomposition of Deacidite FF are observed in both alpha and gamma-radiolyses, the effect being more prominent in the former. The lower the dose rate, the higher is the rate of decomposition.

In many results published in the literature, no mention is made of the salt form of the resin or the dose rate used. It is likely that reactions with H_2O^- and, to a smaller extent, the presence of dose rate effects can explain some of the differences in reported stabilities (Table 5.1.). Most of the data published, are expressed in terms of total capacity loss. Fisher(48) distinguished the salt-splitting capacity and Streat and Hall(15) gave the complete analysis of an irradiated resin by determinations of strong base and weak capacities and individual basic products. The results of gamma-radiolyses of Deacidite FF reported in this work are in agreement with Hall(69), Fisher(48) and Saldadze(19).

Table 5.1.

Anion exchange resin.	Type of radiation.	Dose Mr.	Total capacity loss %.	Strong base capacity loss. %.	Weak base capacity gain. %.	Reference.
Deacidite FF (Cl/OH)	gamma	250	31	50	19	69
Deacidite FF OH.	"	200	25	50	25	69
Deacidite FF NO_3.	"	310	15	50	35	69
Dowex A1	"	360	40	-	-	47
Dowex A1	"	500	50	-	-	66
Amberlite IRA 400	"	210	20	47	-	48
Amberlite IRA 401	"	210	27	50	-	48
AV-17	"	470	85	-	-	19
AM	"	470	94	-	-	19
AV-17	"	190	56	-	-	22
Amberlite IRA 401	n and γ	650	45	-	-	46
I mac S-4	"	570	50	-	-	46
Dowex-1 OH	X-ray	1000	49	-	-	43
Dowex-1 Cl	"	1000	60	-	-	43
Dowex-1	α-particle	600	44	47	-	24
Permutit S-1	"	500	27	38	-	24
Permutit SK.	"	500	17	24	-	24

Ahrens(24) finds that the order of stability of anion exchange resins towards alpha radiation are

Permutit SK > Permutit S-1 > Dowex-1

The G-(decomposition of strong base capacity) over the first 200 Mr. for Dowex-1, a resin similar in structure to Deacidite FF, is 3.8. The G-value for Permutit S1 is 2.5. In this work the G-value for strong base capacity loss for Deacidite FF under various conditions is 4.0-4.5. The somewhat smaller values reported by Ahrens may be due to measurement of capacity being made on a final volume basis. Also the initial capacity differences in these resins are partly responsible for the differences in the rates of reactions. It has been shown that relatively more weak base capacity is produced in alpha radiolysis than in gamma radiolysis. The formation of weak base results in the total capacity reducing less rapidly then the strong base capacity. However, this weak base production may change chemical selectivity and exchange characteristics. A comparative study of the break through capacity of irradiated and unirradiated resins with various isotopes would be useful in assessing the application of ion exchange resins in processing highly radioactive solutions.

All the results of γ-radiolyses and most of the alpha-radiolyses of Deacidite FF show that the decomposition rate is dependent on concentration of functional groups in the resin. The capacity changes and product yields are exponential with increase of dose. The overall decomposition of the resin due to reactions (1) and (2) are parallel first order reactions.

The changes in cross-linking of resins during radiochemical processings will be expected to effect exchange kinetics and column pressure drops. Creed$^{(17)}$ however has shown that the changes in pressure drop in irradiated resins in his systems are small and can be neglected. Experimental work in this thesis has shown that gamma radiation at high doses (above 200 Mr.) increases the cross-linking although under some conditions i.e. irradiation in presence of 7N HNO_3, the resin undergoes decross-linking$^{(16)}$. Alpha radiation in general causes decross-linking of the resin and this is in agreement with the observations made by Ahrens$^{(24)}$. Charlesby$^{(70)}$ has extensively investigated the radiation induced cross-linking and degradation processes in various polymers and reviewed various theories in relating the observed behaviour with radiation dose. He concluded that cross-linking is a more complex process than was first assumed. In ion exchange resins, the loss of functional groups with increasing radiation dose is expected to reduce the swelling weight due to reduction of the water of hydration(7). The increase in swelling weight with increasing alpha dose is therefore explained by the change in number of transverse bridges in the structure of polymer matrix producing modification of the amount of water retained in the internal phase of the resin.

Associated with increase of swelling weight there is an increasing dissolution of polystyrene polymer. In gamma radiolysis of the anion exchange resin, as the polystyrene becomes cross-linked, the solubility decreases. Creed(17) by a diffusion measurement observed a small change of exchange kinetics in irradiated anion exchange resins. An extension of such studies to highly irradiated anion exchange resins would be valuable in assessing exchange kinetics of relevance to radiochemical separation process.

The application of ion exchangers in removal of fission products from reactor core solutions has been proposed by Ferguson(67). Cathers(66) has shown that in the case of a 360-MW reactor, 300 litres of core solution at room temperature can be processed per day to remove 400 g. of gross fission products, provided a 5 days cooling period is allowed. In this case, the solution is to be processed by a 2-litre bed of sulphonated phenolic resins, and the acceptable capacity loss is taken as 10% of the total. A polystyrene resin which suffers a capacity loss of about 15% per watt-hr. per g. resin can be used after 100 days of cooling period.

Experimental work in this thesis shows that Deacidite FF can be used in such a process only to a limited radiation dose. Thus if 10% total capacity loss is acceptable and the swelling weight change is to be kept small, the resin can be used up to about 180 Mr. ($\sim$0.5 watt-hr/g.) for alpha radiation. For γ-irradiations, the resin in most forms can be used up to 40-50 Mr. but the nitrate form of resin can be used to a radiation dose in excess of 100 Mr. Therefore, if the contact time of the absorbed isotope is small, these conditions are quite acceptable for many processes e.g. of Pu.239 (specific power 0.0019 watts/g. Pu)(66). Account must be taken of other activities in the process solution, and in primary separations these will contribute largely to resin decomposition.

LIST OF FIGURES.

(List of Figures - contd.).

(List of Figures - contd.).

Symbols and Abbreviations Used.

Å	Ångström unit (= 10^{-8} cm.).
d.p.s.	Disintegrations per second.
DVB	Divinylbenzene.
ev	Electron-volt.
ϵ	Molar extinction coefficient (litre/mole cm.).
E	Energy of a particle (Mev).
G-value	Number of molecules changed per 100 ev of energy absorbed.
g.	gram.
H_2O^-	Hydrated electron.
$lb/\square^2$	Pounds per square inch.
Kd	Distribution coefficient.
M	Molarity.
Mev	Mega electron-volt (10^6ev).
meq/g.	Milliequivalent per gram resin.
Mr.	Megarad (10^6 rads).
N	Normality.
O.D.	Optical density.
R	Range of alpha particles in matter (mg/cm^2).
SB	Strong base.
t	temperature ^{o}C.
w	Weight fraction of the elements of which a compound is composed of.
WB	Weak base.
Z	Atomic number.
λ	10^{-3} ml.

Appendix 1.

Calculation of the range of americium alpha-particles in Deacidite FF and in the resin slurry.

The ratio of the range in an absorber R_z and the range in air R_a for alpha particle energy E is given by equation (72)

$$\frac{R_z}{R_a} = 0.90 + 0.0275z + (0.06-0.0086z) \log \frac{E}{M} \qquad \ldots (1)$$

where M is the mass number of the particle, E is the initial energy of the particle in Mev, and z = atomic number of absorber. This equation is applicable to absorbers with $z > 10$. For lighter elements, $(0.90 + 0.0275z)$ of equation (1) is replaced by 1.00 except for helium and hydrogen where values of 0.82 and 0.83 are used.

The range of alpha particle of energy 5.46 Mev in air is 3.85 mg/cm.^{2} (72). Using the equation (1) the range of the alpha particle in hydrogen

$$R_H = 3.85\ (0.30 + 0.051 \log \frac{5.46}{4}) = 1.18 \text{ mg/cm}^2.$$

The range in oxygen

$$R_O = 3.85\ (1 - 0.008 \log \frac{5.46}{4}) = 3.85 \text{ mg/cm}^2.$$

The range in carbon

$$R_C = 3.85\ (1 + 0.008 \log \frac{5.46}{4}) = 3.85 \text{ mg/cm}^2.$$

The range in nitrogen

$$R_N = 3.85\ (1 - 0.0002 \log \frac{5.46}{4}) = 3.85 \text{ mg/cm}^2.$$

The range in chlorine

$$R_{Cl} = 0.90 + 0.0275 \times 17 + (0.06-0.00086\times17) \log\frac{5.46}{4})$$
$$= 5.2 \text{ mg/cm}^2.$$

The range of alpha particle in a compound R_t is given by

$$\frac{1}{R_t} = \frac{w_1}{R_1} + \frac{w_2}{R_2} + \frac{w_3}{R_3} \qquad \ldots (2)$$

where w_1, w_2, w_3 are the weight fractions of elements of which the compound is composed of.

Water is 88.9% by weight of oxygen and 11.1% by weight of hydrogen and hence from equation (2)

$$\frac{1}{R_{H_2O}} = \frac{0.889}{3.85} + \frac{0.111}{1.18}$$, so that

$R_{H_2O} = 3.07$ mg/cm^2. or the range is 3.07×10^{-3} cm.

Similarly, in Deacidite FF, the weight fractions of carbon, hydrogen, **nitrogen** and chloride are 0.70, 0.096, 0.34 and 0.17 respectively, so that

$$\frac{1}{R_{resin}} = \frac{0.70}{3.85} + \frac{0.096}{1.18} + \frac{0.034}{3.85} + \frac{0.17}{5.2} = 0.3046$$

or

$R_{resin} = 3.28$ mg/cm^2. or range = 3.28×10^{-3} cm.

and range in a resin slurry of 50% H_2O and 50% resin

$$= \frac{1}{R_{slurry}} = \frac{0.5}{3.07} + \frac{0.5}{3.28} = 0.3187$$

$$R_{slurry} = 3.14 \times 10^{-3} \text{ cm.}$$

Appendix 2.

Calculation of alpha dose received by the resin slurry.

Alpha-particle dose received by the resin was calculated from the known quantities of the americium and resin slurry in the system. In systems where initial weight of dry resin and the amount of americium solution was known, the dose was calculated as follows:-

Am-241 = x mg.

Resin = y g.

Solution = z g.

Specific activity of Am-241 = 1.19×10^8 d.p.s. per mg.

Energy of each alpha-particle = 5.46 Mev.

Dose rate/day mg. of Am. = $(5.46 \times 1.19 \times 10^8 \times 3600 \times 24)$ Mev.

$\therefore$ Dose rate/day/x mg.Am. = $(5.46 \times 1.19 \times 10^8 \times 3600 \times x \times 24)$ Mev.

Since this dose has been received by $(y+z)$ g.

The dose rate in the system =

$$\frac{5.46 \times 1.19 \times 10^8 \times 3600 \times 24 \times x}{(y+z) \times 6.2 \times 10^{13}} \text{ Mr/day.} \qquad \ldots (1)$$

In systems where z was not initially known, the apparent volume and density of the slurry were experimentally determined, so that the weight of the slurry per g. of dry resin was known.

Example:

0.2888 g. dry (SCN)form of resin slurried in 5M NH_4SCN solution occupies 0.7 ml.

The density of such slurry = 1.09 g./ml.

$\therefore$ weight of 1 g. dried SCN$^-$ form of resin slurried in

$$5M\ NH_4SCN = \frac{0.700 \times 1.09}{0.2888}\ g.$$

The dose rate was then calculated by using the equation (1) above.

It has been assumed that all the energy was absorbed in the system in fact, however, Ahrens(24) has calculated that about 16% of the energy is lost through the surface.

Appendix 3.

Dosimetry in irradiations of Deacidite FF by Co-60 gamma-rays.

The molecular weights of ion exchange resins are not precisely known, however each repeating unit of the resin containing a functional group may be taken as a molecule. The molecular weight of such a unit containing 8% DVB is 192. However the molecular weight changes with exchangeable ions i.e. Cl^-, NO_3, $SO_4^{=}$, etc. Calculations (Table A.3.1.) show that numbers of electrons per g. resin in the various forms are almost equal to that of water. The Fricke dosimeter is therefore applicable for calculation of dose received by a resin slurry when irradiated by gamma-rays.

The dose received by the Fricke dosimeter is calculated as follows:-

The measured optical density O.D. = $\varepsilon c d$

where ε is the extinction coefficient = 2115 at 20°C.

c = concentration of Fe^{3+} in moles per litre.

d = cell thickness in cm. = 1 cm.

Above 20°C., O.D. decreases by 0.7% per °C. increase in temperature, so that
$$c = \frac{O.D.(1-0.007t)}{2115}$$
where t is the temperature of the sample minus 20°C.

Table A.3.1.

Compound	Molecular weight*.	Number of electrons per molecule.	Number of electrons per g. x 10^{23}.
Water	18	10	3.34
Chloride form of resin.	208	113	3.23
Nitrate form of resin.	235	128	3.28
Thiocyanate form of resin.	231	126	3.28
Sulphate form of resin.	221	121	3.30

*8% DVB is taken into account.

The energy absorbed is then calculated from

$G\ Fe^{3+} = 15.5$ and assuming the density of the solution as unity,

$$\text{Energy absorbed} = \frac{100 \times 6.02 \times 10^{23} \times c}{15.5 \times 10^{3}} \text{ ev/g.}$$ ✓

Substituting the value for c,

$$\text{Dose absorbed in rad} = \frac{100 \times 6.02 \times 10^{23} (1-0.007t) \text{ O.D.}}{15.5 \times 10^{3} \times 6.24 \times 10^{13} \times 2115}$$

$$= 2.94 \times 10^{4} (1-0.007t) \text{ O.D.}$$

Appendix 4.

Calibration for recovery of amine by steam distillation.

2-15 ml. of 10^{-2}N aqueous trimethylamine solution was transferred to a 50 ml. steam distillation flask. 2 ml. of conc. NaOH was added. The trimethylamine was steam distilled. The distillate was made up to 25 ml. and the amine recovered was estimated by the picrate method. The recovered amine against initial quantities of amine are plotted, (Fig.A.4.1.). The procedure was repeated with the amines produced by γ-radiolysis of $\sim$ 0.1 g. of chloride resin. The leach solution was made up to 25 ml., 12.5 ml. was used for estimation of amine prior to distillation while the remaining 12.5 ml. was steam distilled. The calibration curve is reproducible by ± 10% and shows that 50-80% of the amine is recovered by steam distillation.

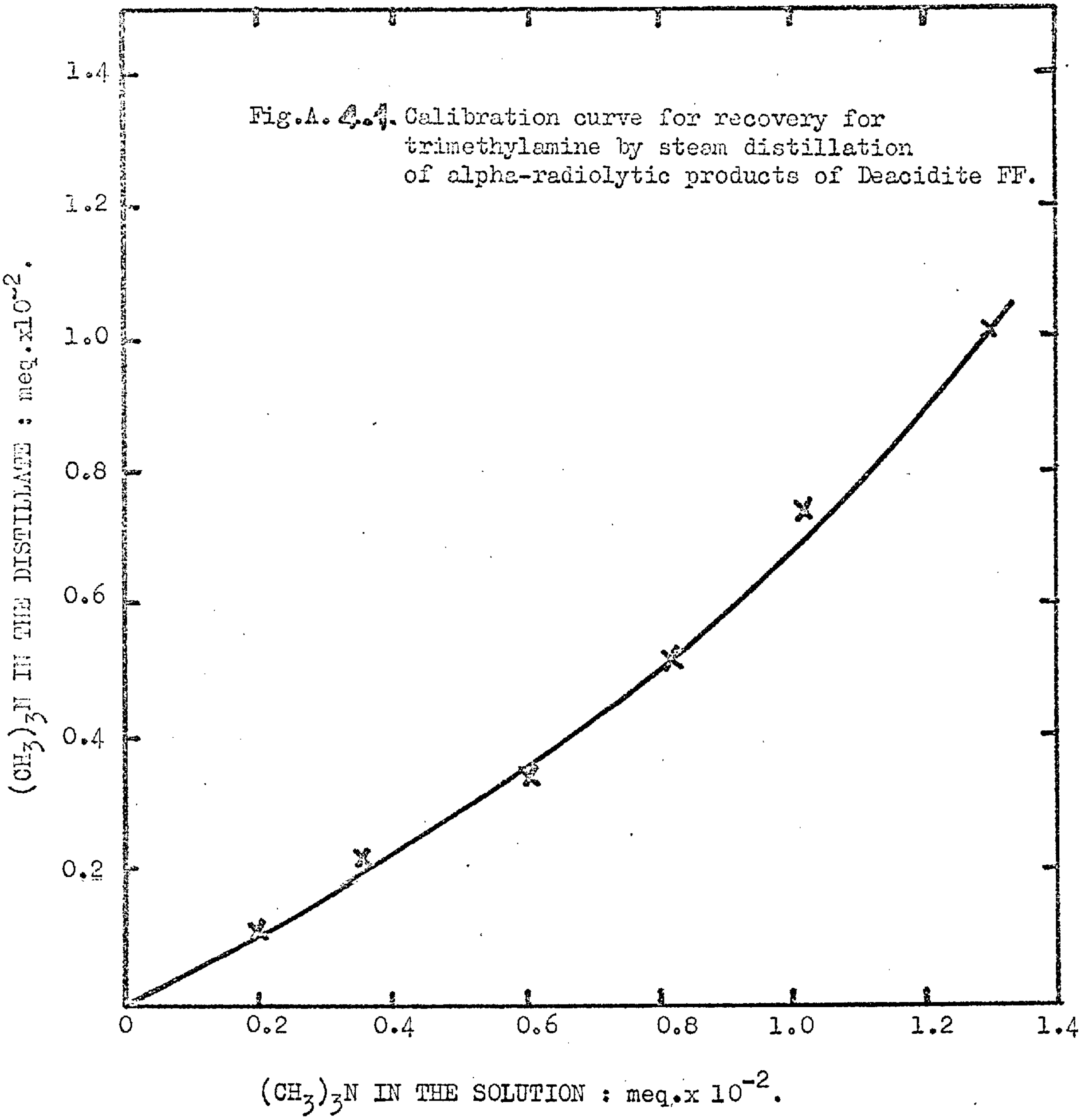


Fig.A. 4.4. Calibration curve for recovery for trimethylamine by steam distillation of alpha-radiolytic products of Deacidite FF.

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